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ABSORPTION COEFFICIENTS OF SEVERAL ATMOSPHERIC GASES

K. WATANABE

MURRAY ZELIKOFF

EDWARD C. Y. INN

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page 24	line 14	B^2 state	change to	$B\,^2\Sigma_g^-$ state
page 44	line 8	$^1\Sigma_g^+ \to (\Pi_g)^{-1}\sigma_g,\,^1\Pi_g$	change to	$^1\Sigma_g^+ \to (\pi_g)^{-1}\sigma_g,\,^1\Pi_g$
page 60	line 5 from bottom	10.12 ± 0.05 ev	change to	10.13 ± 0.02 ev
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ABSTRACT

Absorption coefficients, k, of O_2, O_3, CO, CO_2, NO, N_2O, N_2, H_2O, H_2, CH_4, and NH_3 were measured in the spectral region from 1050 to 2500 Å.   Using a linear photoelectric detector and an absorption cell at the exit slit of a vacuum monochromator, the improved method eliminated systematic errors.   Several thousand k-values were determined and a number of new bands and continua were found.   Energy states and dissociation limits are discussed.   The ionization potentials of NO and NH_3 were found to be 9.23 ev and 10.12 ev, respectively, by measuring the long wavelength limit of the ionization continuum.   Ionization cross sections of NO in the region from 1080 to 1345 Å were obtained.   Some of the data were applied to the formation of the D layer.

FOREWORD

Today the sights of the Air Force are being focused toward higher and higher altitudes. Altitudes which appear fantastic today will become the operational altitudes in the next ten years. With these altitudes come problems which are quite different from those with which we are accustomed at the conventional altitudes of today. At altitudes of 50 miles or higher, we enter into an entirely new realm of the atmosphere which many prominent scientists like to call the chemosphere. It is a region of intense ultraviolet radiation from the sun, and because of this huge influx of energy, it is a region of chemical change and radical reactions. Constituents of our atmosphere, which we are accustomed to consider as stable near the earth's surface, become readily dissociated and recombine to form compounds with vastly different properties. Some of these gases are deadly poisons, some of these have violent effects upon the combustion processes of reciprocating and jet engines, and others are corrosive to metal and plastic components of an aircraft. Although these gases are present in very dilute concentrations, it quite possible that supercharging will increase the concentration to the danger point. Such problems seem somewhat remote today, but we must realize that considerable time is required to acquire information for the future in regions of the atmosphere which are presently accessible only to occasional rocket flights of very short duration. In order to study these phenomena at short range, the more fruitful approach has been to synthesize these conditions in the laboratory through the use of known mixtures of pure gases that are irradiated by ultraviolet light of wavelengths comparable to those which exist in the chemosphere. Reactions can then be studied under controlled conditions and the role of each constituent can be determined.

This paper represents the first step in such an approach to the chemistry and composition of the high upper atmosphere. Absorption cross sections of atmospheric constituents in the vacuum ultraviolet is a basic property which is the foundation of all gaseous photochemical reactions. Up to the present time the state of knowledge of absorption of atmospheric gases in the vacuum ultraviolet has been spotty and, in several cases, quite inaccurate. The work described in this paper represents the first successful determination of continuous values of absorption coefficients of atmospheric gases in the wavelength region down to 1050 Å by the use of a photoelectric method. The work has been carefully done, and is of sufficient caliber to justify extension of the present absorption coefficients in the International Critical Tables down to 1050 Å. At the present time the information is of primary interest to geophysicists, physicists and photochemists interested in high altitude phenomena, but it is highly probable that in the not too distant future, it will represent one of the fundamental stepping stones upon which we shall build the Air Force of the future.

P. H. WYCKOFF
Chief, Atmospheric Physics Laboratory

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ABSORPTION COEFFICIENTS OF SEVERAL ATMOSPHERIC GASES *

1. INTRODUCTION

The composition of the atmosphere in the region above the troposphere is affected by a number of processes such as mixing, diffusion, photochemical and recombination processes. When sufficient data are available, it is possible to deduce reliable information on atmospheric constituents and penetration of solar radiation, and this can be done well in advance of direct measurements. For example, many years ago Chapman (1930) made a calculation to show the existence of a transition layer of atmospheric composition due to the process

$$O_2 \rightarrow O + O,$$

at an altitude of about 100 km, but only recently direct measurements have become possible at this altitude. At higher altitudes the determination of atmospheric composition by direct methods becomes increasingly difficult because of low atmospheric densities. Moreover, at these heights the constituents are likely to be in unstable or excited states, so that gas samples cannot be brought down to the laboratory in these conditions.

Most of the primary photochemical processes occurring in our atmosphere are expected to be induced by solar radiation of wavelengths below about 2800 Å, which is completely absorbed in the atmosphere. This is clear from the fact that the constituents of air are rather stable molecules that require energetic photons to produce photodissociation and photoionization. The importance of extreme ultraviolet radiation has been long recognized in connection with the various atmospheric layers; however, a number of recent calculations on the formation of these layers have led to diverse conclusions. For example, some of the processes suggested or invoked for the formation of the D layer are: photoionization by X-rays, photoionization of molecular oxygen in the region from 900 to 1000 Å, ionization of metastable atomic oxygen by Lyman alpha (1216 Å) in two steps, photoionization of nitric oxide in the region from 1100 to 1300 Å, and photoionization of sodium in the spectral region from 1800 to 2400 Å. This example of the freedom exercised in the choice of process illustrates the need for data on various parameters such as the intensity distribution of the solar, extreme ultraviolet spectrum and absorption cross sections of atmospheric constituents.

The intensity of absorption is expressed here by the absorption coefficient k in reciprocal centimeters, or by the absorption cross section, σ in square centimeters. The former is defined by the equation

$$I = I_0 \exp(-kx),$$

where I_0 and I are the incident and transmitted light intensities and x (in centimeters) is the layer thickness of the absorbing gas reduced to NTP. The cross section is defined by

$$\sigma = \frac{k}{n_0},$$

where n_0 is the number of particles per cubic centimeter at NTP. If the k-values are known throughout the spectral region covered by a particular electronic transition, the oscillator strength (or f-value) of this transition can be computed by

$$f = \frac{mc^2}{\pi e^2 n_0} \int_{\nu_1}^{\nu_2} k_\nu d\nu,$$ (1)

where m and e are the electronic mass and charge, c is the velocity of light and ν is the wave number in reciprocal centimeters.

Absorption coefficients of several atmospheric gases have been measured in the vacuum ultraviolet by a number of investigators. Ladenburg and van Voorhis (1933) made the first quantitative measurement of absorption intensity and obtained k-values for O_2 in the region from 1330 to 1670 Å of the Schumann-Runge continuum. Schneider (1940) obtained data for dry, CO_2-free air at 350 wavelengths in the region from 380 to 1600 Å but his low k-values were only estimates. Preston (1940) determined the absorption coefficients of N_2, O_2, CO_2, and H_2O at Lyman alpha (1216 Å) but disagreed with the data on O_2 obtained by Williams (1940) by a large factor. The absorption coefficients of CH_4, CO_2 and H_2O in the region above 1400 Å were obtained by Wilkinson and Johnston (1950). More recently, similar data were obtained for NO and N_2O in the region above 1400 Å by Mayence (1952). Clarke (1952), Weissler, Lee and Mohr (1952) and Weissler and Lee (1952) reported data for both O_2 and N_2 at a number of wavelengths in the difficult region below the transmission limit of LiF. At two wavelengths where comparisons can be made, their results agreed for O_2, but not for N_2. There appear to be no data for O_3, CO and NH_3 and many wide gaps are still present in the available data.

For a number of reasons, measurements of absorption coefficients are more difficult in the vacuum ultraviolet than at longer wavelengths. First of all, the lack of a light source with continuous spectrum seriously limits measurements of sharp bands with rotational structure. The hydrogen discharge tube provides a continuum down to about 1650 Å. Below this wavelength, available sources for intensity measurement give only line spectra; condensed discharges of the Lyman type are too erratic for photometry. Other inconveniences are inefficiency of gratings due to poor reflectivity, scarcity of suitable optical material and detectors, and the necessity of preparing gases of high purity.

The main purpose of this paper is to present absorption coefficients of several atmospheric gases in the spectral region from 1050 to 2500 Å. Most of the data have not yet been published, except a brief note by Watanabe, Inn and Zelikoff (1952). The experimental techniques and arrangement, which are somewhat different from those used by previous investigators, are described in detail. In addition to absorption coefficients, new data obtained on the absorption spectra (bands, continua), dissociation energies and ionization potentials are presented. The application of some of the data to the theory of the formation of the D layer is also briefly reported. Some of the data are of a preliminary nature, and refinement must depend on improvement of experimental techniques, particularly in the optical resolution.

2. EXPERIMENTAL

Apparatus and experimental techniques used in vacuum spectroscopy are described in a book by Bomke (1937) and a review by Boyce (1941). After 1941, the activity in the field was more or less reduced to a
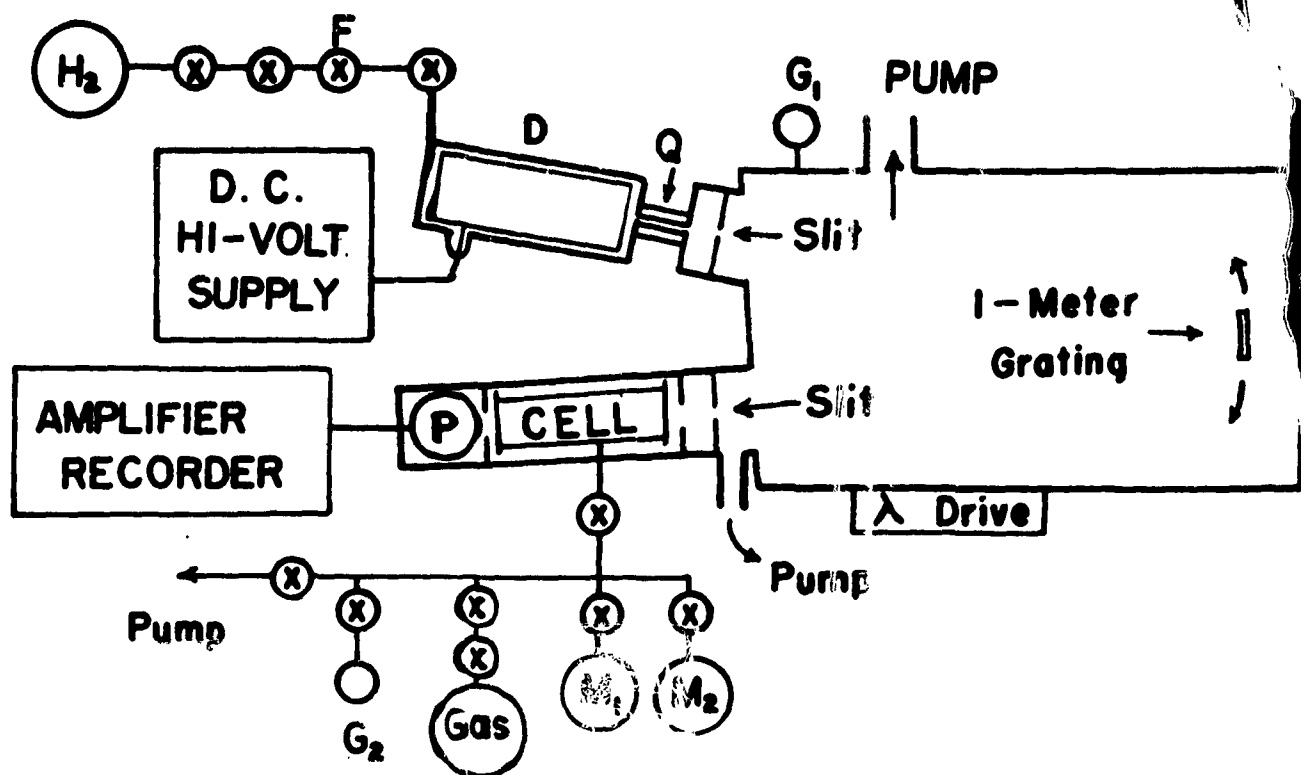
Fig. 1. Experimental arrangement for the absorption measurement.

few groups of investigators who were primarily interested in molecular spectra, and very few advances in experimental technique have been made as compared to the advances in infrared spectroscopy.

To overcome some of the uncertainties common to absorption photometry in the vacuum ultraviolet attempts were made to improve the techniques and experimental arrangements used by others. A vacuum monochromator was used instead of a spectrograph so that it was possible to place an absorption cell with LiF windows at the exit slit. This arrangement greatly minimized photodecomposition of the absorbing gas. In place of photographic plates, a phosphor-coated photomultiplier was used as a detector; thus, the labor of analyzing the absorption data was greatly reduced. To insure the purity of gas samples, each gas was analyzed with a mass spectrometer.

The experimental arrangement employed in the present work is shown schematically in Fig. 1. Most of this has been reported by Watanabe and Inn (1953); however, for convenience, the description of the apparatus and experimental procedure, including some of those used by others, are described in the following sections.

2.1. LIGHT SOURCE

There appears to be comparatively little progress in the development of light sources suitable for photometry in the vacuum ultraviolet. Lee and Weissler (1952) reported a low-pressure spark which was used for their photographic measurement of absorption intensities in the region from 300 to 1300 Å. The constancy of this light source is claimed to be about 2 percent; however, the source provides a line emission

spectrum. Carpenter (1952) of Baird Associates has investigated the development[*] of several light sources suitable for use in the vacuum ultraviolet. Major emphasis was in the development and construction of high-intensity, hot-cathode, xenon lamps for use in the study of photochemistry in the Schumann region. Among the other types of lamps constructed, the electrodeless lamp excited by microwaves showed considerable promise. This type of lamp was also investigated by Zelikoff, Wyckoff, Aschenbrand and Loomis (1952). They used metal vapors to obtain strong emission lines for photochemical reactions.

In the present work, the light source (D in Fig. 1) was a windowless hydrogen discharge tube with a quartz capillary (Q) and was operated at about 600 v $\times$ 0.4 amp DC. Similar light sources were previously used by Powell (1934), Little (1946), Johnson, Watanabe and Tousey (1951). Tank hydrogen was used without purification and its flow rate was kept constant by means of a needle valve and a simple flow meter (F in Fig. 1). The pressure in the main chamber of the monochromator was held at about 1×10^{-4} mm Hg when the light source was in operation. The constancy of the discharge condition was checked by the arc current, the flow rate and the ion gauge (G$_1$). As a rule, the light intensity did not vary more than a few percent over a period of several hours. This was the largest source of error; however, when a more accurate result was desired, repeated measurements were made at fixed wavelengths.

2.2. DETECTOR AND ITS CALIBRATION

The method of photographic photometry has been employed almost exclusively in the past for measurement of absorption coefficients in the vacuum ultraviolet; however, Preston's experiment (1940) is an exception. He used an argon-filled platinum photocell with an LiF window for his measurement at Lyman alpha. In view of the well-known uncertainties of photographic plates, particularly for use in the region below 2000 Å, a photoelectric method was selected.

Perhaps because of the lack of optical materials for use as envelopes, photoelectric detection has not been used often in the region below the transmission limit of quartz. Powell (1934), Preston (1940) and Little (1946) used gas-filled, platinum photocells. More recently, Parkinson and Williams (1949) used a phosphor-coated photomultiplier to measure down to 1450 Å, and Bolton and Williams (1952) down to 970 Å. To find the best coating material for photomultipliers, Johnson, Watanabe and Tousey (1951) studied the relative quantum efficiencies of a number of fluorescent materials in the region from 900 to 2500 Å with several types of photomultipliers. This work was based on energy measurements by Packer and Lock (1951). Their work was extended to 584 Å by Watanabe and Inn (1953). Gyorgy and Kingston (1951) reported successful use of a beryllium-copper photomultiplier without envelope in the spectral region from 50 to 1000 Å. Photoelectric yield of several metals in the vacuum ultraviolet was investigated without spectral dispersion by Kenty (1933). Baker (1938) obtained data for photoelectric yield of cadmium down to 1000 Å, but his energy measurements were indirect. Recently, Hinteregger and Watanabe (1952) obtained the photoelectric yield of platinum, tungsten and nickel in the region from 850 to 2000 Å and at 584 Å, using a vacuum monochromator and direct energy measurements with a thermocouple. They obtained reproducible results with windowless photocells. Similar measurements were reported by Wainfan
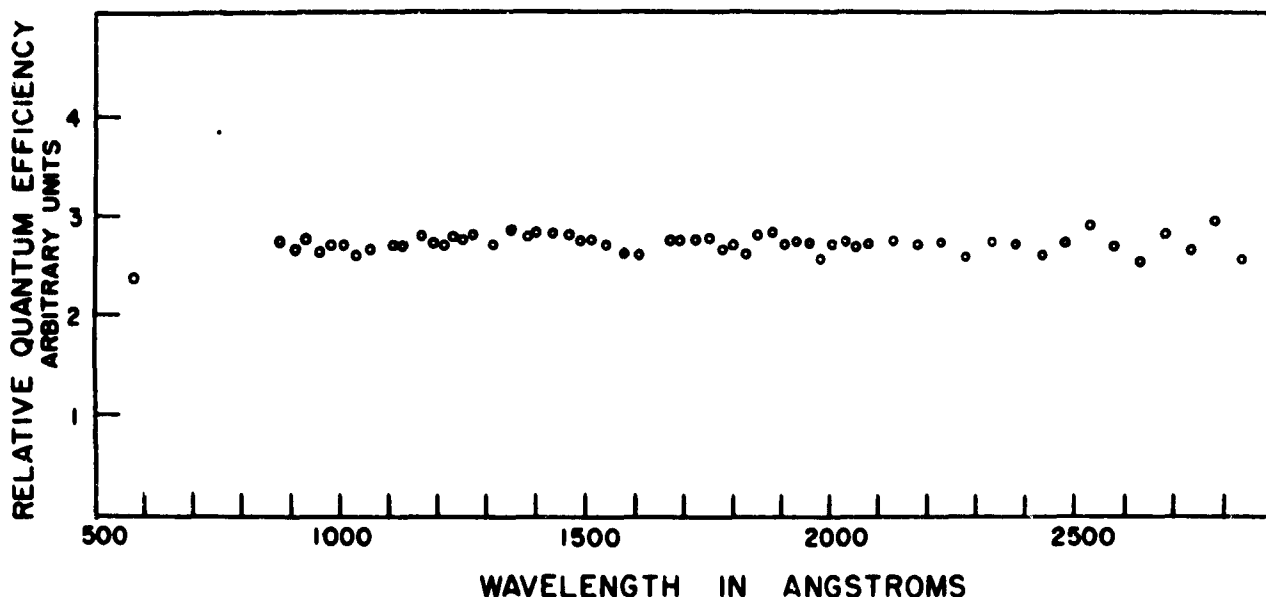
Fig. 2. Relative quantum efficiency of sodium salicylate.

and Walker (1952). The possibilities of sensitive photon counters appear promising, although the reproducibility does not seem adequate at present. They have been used by Fujioka and Ito (1951), Friedman, Lichtman and Byram (1951).

In the present work, a 1P21 tube coated with sodium salicylate was used as a detector. From a number of fluorescent materials tested, sodium salicylate was selected as the best material for use with a photomultiplier. Unlike most organic fluorescent materials, it did not sublime in vacuum and remained stable over many months. Unlike every inorganic phosphor tried, its response was uniformly excellent over the entire spectral region from 500 to 3000 Å.

The response of the sodium salicylate was found linear with intensity by direct comparison with the thermocouple response at a number of wavelengths. A windowless, compensated thermocouple was used as the radiation detector for absolute energy, i.e., as the standard for calibration of the phosphor-coated photomultiplier. The thermocouple response was amplified by a Liston-Becker, breaker-type amplifier and fed into a Speedomax recorder. The thermocouple sensitivity in air, as measured with a standard lamp from the National Bureau of Standards, was 0.076 microvolt per microwatt. The sensitivity in vacuum, however, under the usual operating conditions was found to be 1.31 μ volt/μ watt when helium was used and 1.35 μ volt/μ watt when hydrogen was used in the discharge tube. A more complete description of the calibration was reported by Watanabe and Inn (1953).

Comparison of thermocouple and photomultiplier was made over an intensity range of a factor of 50 by selecting different lines and varying the current of the light source. The largest intensity used was about 2×10^{13} quanta cm^{-2} sec^{-1}. The linearity of the detector response simplified quantitative absorption measurements and minimized systematic errors.

To determine the relative quantum efficiency of sodium salicylate, type 1P21 tube was found preferable to type 5819. The latter gave a lower scattered light-to-signal ratio, as expected from the geometry of its photocathode. The proximity of its photocathode to the phosphor was undesirable, however, since the

light beam moved a little as the spectrum was scanned and a non-uniformity in the sensitivity of the photo-cathode became a source of error. The relative quantum efficiency was obtained by direct comparison with thermocouple measurements. The result is shown in Fig. 2. The ordinate is proportional to $I_p/I_t\lambda$ where I_p is the photomultiplier current, I_t is the thermocouple response and λ is the wavelength in angstroms. The points fall nearly on a horizontal straight line, thus showing constant quantum efficiency. At the 584 Å line of helium the quantum efficiency appears to be about 15 percent lower than at longer wavelengths. Two of the 1P21 tubes coated with sodium salicylate were stored as secondary standards, after they were calibrated against the thermocouple under specified conditions. One of them was later used for determination of the photoionization yield of nitric oxide.

In most of the absorption measurements, the photomultiplier (P in Fig. 1) was used with dynode voltages from 70 to 90 volts, depending on the intensity of the beam for different spectral regions. The current of the photomultiplier was amplified by an RCA ultrasensitive microammeter (type WV84A), and then fed into a Speedomax recorder.

2.3. MONOCHROMATOR

Rather few monochromators have been built and used in the vacuum ultraviolet. Baker (1938) used a monochromator for his study of photoelectric yield. Parkinson and Williams (1949), Johnson (1952) and others have used monochromators of the type in which the grating was simply rotated about a fixed point on the Rowland circle. Fujioka and Ito (1951) and Baird Associates have built normal incidence monochromators in which the grating moves along the Rowland circle. The type manufactured by Baird Associates was described by Tousey, Johnson, Richardson and Toran (1951).

The dispersing instrument used in the present work was a Baird 1-m (15,000 lines per inch), normal-incidence, vacuum monochromator. For the absorption measurements, a slit width of 50 microns was used for both slits (see Fig. 1). This corresponded to a bandwidth of 0.85 Å and the resolution was about 1 Å, which is believed to be the best yet obtained with a vacuum monochromator. The spectrum was scanned at 20 Å per minute and wavelengths were measured to the nearest half angstrom. Occasionally, the wavelength reading was in error by as much as two angstroms. For thermocouple measurements, it was necessary to use a wide slit (1 mm). The thermocouple was mounted directly on the slit mount which could be rotated, and its sensitive area, 1×3 mm, served as the slit.

The pumping system consisted of a Kinney mechanical pump and a 6-in. oil diffusion pump. The best vacuum obtained in the main chamber of the monochromator was about 1×10^{-6} mm Hg; normally, it was about 2×10^{-5} mm.

2.4. GRATING

Gratings are, in general, inefficient in the vacuum ultraviolet, primarily because of poor reflectivity. There is no doubt that progress in blazing technique can improve the efficiency of gratings, but the possibility of finding coating materials of good reflectivity cannot be excluded.

A rather striking phenomenon which occurred during the thermocouple measurements was the great
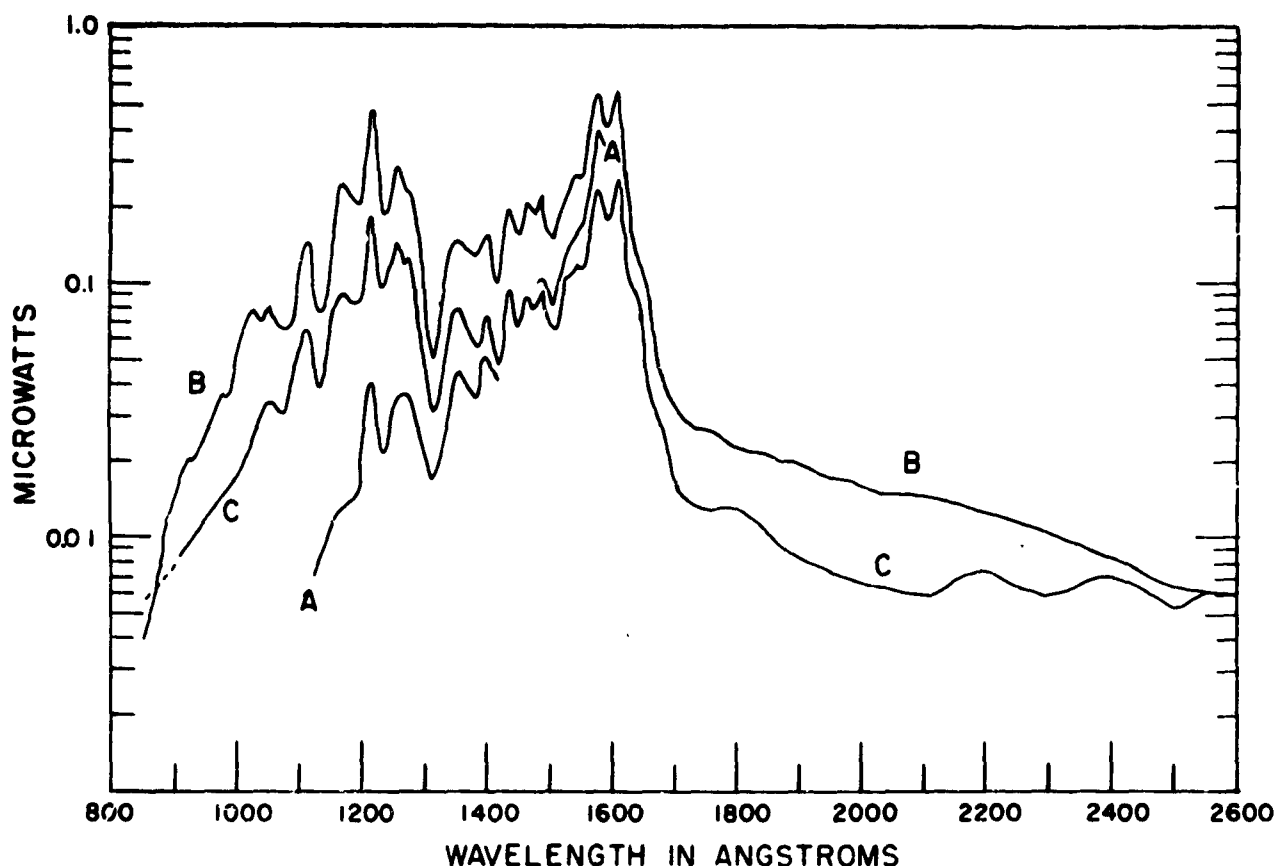
Fig. 3. Spectral intensity distribution at the exit slit of the monochromator.

increase (up to a factor of 30) in the observed spectral intensity, the greatest increase being at the shorter wavelengths. In Fig. 3, curve A represents our first thermocouple measurements of the H_2 spectrum using 1-mm slits. Curve B represents the result obtained after a major change had occurred and the observed intensity had reached a nearly stationary value. In this case, it was possible to measure the H_2 spectrum with the thermocouple down to 850 Å. The 584 Å line of helium was also measured. The unexpected phenomenon was ascribed to an increase in the grating efficiency, as a result of an unintentional coating of the grating with platinum evaporated from the capillary of the light source. This conclusion was made on the basis of eliminating several other possible explanations, such as changes in the detector sensitivity and light source and absorption by gases in the optical path. A proposed explanation that the improvement of the grating resulted from some sort of conditioning in the vacuum system, rather than from the coating, seems untenable, because a second grating which received no coating did not improve while in vacuum over a period of several weeks.

In view of the fact that the improved grating has retained its efficiency, it appeared worth while to duplicate the result. For this purpose, the second grating, which showed poor reflectivity, was sputtered with platinum in vacuum. The first coating of about 400 Å did not improve it, but when the layer thickness was increased to about 1600 Å, the efficiency was found to be greatly improved. The amount of scattered light originating from the grating did not change appreciably, and the resolution, at least in terms of the slit width (0.05 mm) used, was not affected. The results for the two gratings (unintentional coating

on the first one) are shown briefly in Table 1, where R is the factor by which the grating efficiency was increased by platinizing. As anticipated, both gratings showed a somewhat reduced efficiency for wavelengths above 1600 Å. The gain made in the region from 1600 to 1100 Å was rather surprising, however, since Sabine (1939) has shown that aluminum reflects better than platinum in this region. It is possible that the reflectivity of aluminum in this spectral region varies widely and may be reduced by aging. Furthermore, it should be noted that the effective blaze angle of a grating must play an important role.

Table 1. The factor (R) by which grating efficiency was increased by platinizing.

Wavelength (Å)	1650	1600	1500	1400	1350	1216	1100
R for first grating..........	0.8	1.1	1.5	2	2.5	14	25
R for second grating.........	1.0	1.6	7	14	20	13	

An immediate application may be made in rocket spectroscopy for the solar spectrum below 2000 Å. Present efforts appear to be directed mostly to sun-followers that would provide longer exposure time. Since scattered light becomes a problem for long exposure time, it seems worth while to explore the possibility of improving the efficiency of spectrographs. For example, platinized or freshly aluminized gratings might be used to photograph the solar extreme ultraviolet.

2.5. ABSORPTION CELL AND GAS-FILLING SYSTEM

In the region down to the transmission limit of LiF, it is preferable to enclose the absorbing gas in a cell, rather than to use the spectrograph chamber which is usually in communication with the light source. In the former case, pressures of the absorbing gas can be more readily controlled over a wide range, and contamination of the absorbing gas, as well as changes in the spectral characteristics of the light source and grating reflectivity, can be minimized. By varying the pressure in the cell, it is possible to measure absorption intensity covering a range of 10^5 or more.

All of the investigators referred to in Section 1 placed their absorption cell between the light source and the entrance slit, or filled their spectrograph with the absorbing gas. As observed by Ladenburg and van Voorhis (1933), photochemical change of the absorbing gas is quite possible when the cell is near the light source. Moreover, the transmission of the cell window may change because of sputtering and formation of color centers. Therefore, the absorption cell was placed at the exit slit where the number of photons passing through per hour was estimated from our thermocouple data to be at least a few orders of magnitude less than the number of molecules. A pyrex cell (diameter 2.5 cm, and length 4.7 cm) with LiF windows was used for the absorption measurement. For some photoionization measurements a similar cell (6.8 cm long) with electrodes made of parallel strips of platinum was used. The platinum strips were located near the inner wall of the cell and outside the light beam emerging from the exit slit. Electrical leads were provided from the platinum strips to the external measuring circuit. For both cells, cleaved LiF plates about 1 mm thick were used instead of lenses, since the divergence of the beam was small and good transmission was desirable.
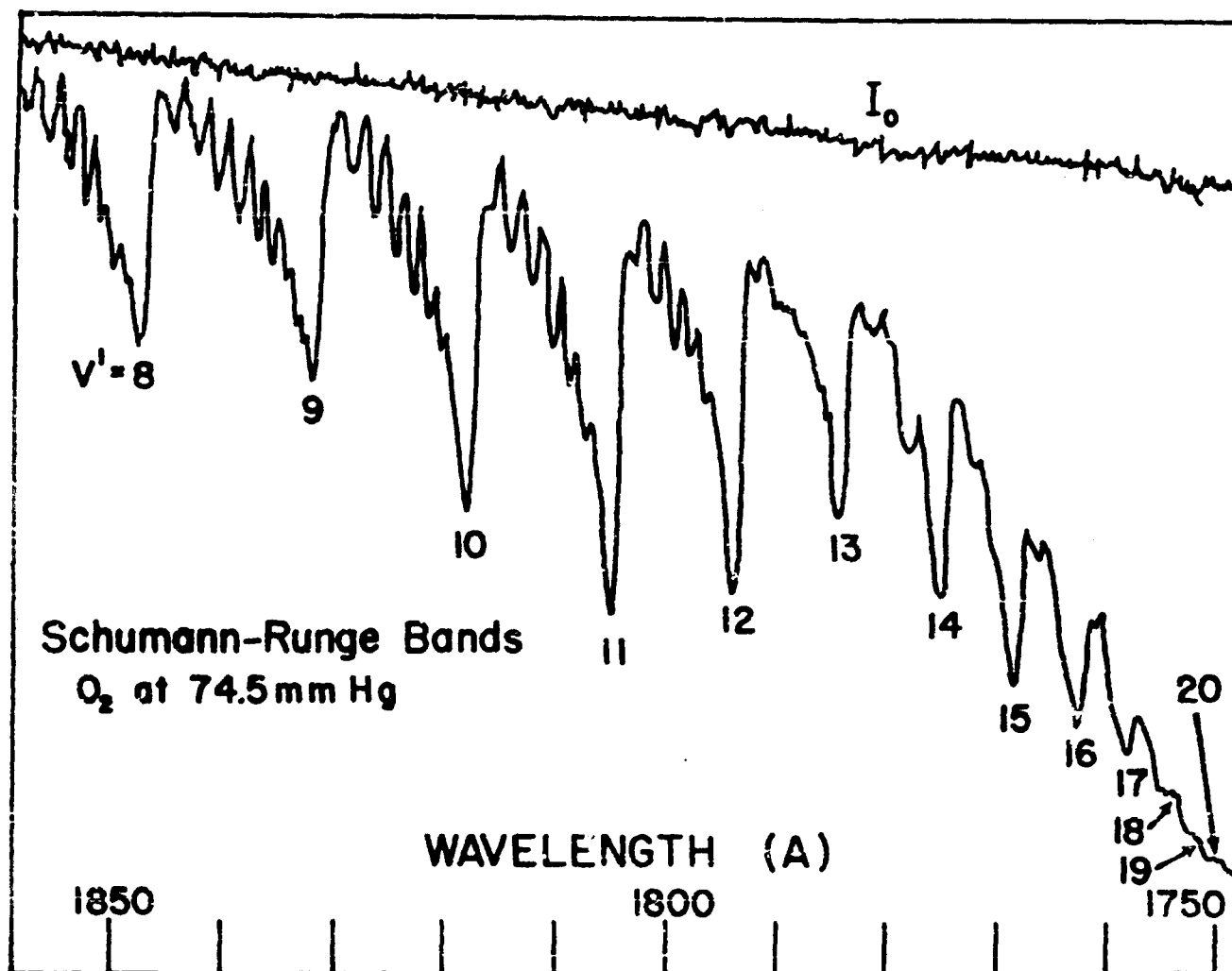
Fig. 4. Recorder trace of the Schumann-Runge bands ($v' = 8$ to $v' \sim 20$).

The gas-filling system (see Fig. 1) was in direct communication with the absorption cell. The system was provided with two McLeod gauges (M_1 and M_2), an Alphatron gauge, mercury manometer, and an ion gauge (G_2). Provisions were made for removal of gas samples for mass-spectrometric analysis. Some of the details are not shown in Fig. 1.

2.6. PROCEDURE

After purification of the gas to be studied, the experimental procedure was as follows. First, a sample of gas was removed directly from the gas-filling system and analyzed for possible contamination using a Consolidated Mass Spectrometer (Model 21-103). Second, the absorption cell was evacuated to about 10^{-6} mm Hg and by scanning the H_2 spectrum, the spectral intensity was obtained as a recorder trace of the photomultiplier current. Third, the cell was filled with the absorbing gas at a suitable pressure and the photomultiplier response of the transmitted light was recorded on the same trace using an ink of different

color. The second and third steps of the procedure were repeated using various pressures to cover the absorption intensities and to determine whether Beer's law held.

To obtain the absorption coefficients from the recorder traces, corrections were made whenever necessary for the scattered light and the fluorescence of the LiF windows. These were, as a rule, small corrections. Several hundred wavelengths, 1 to 5 Å apart, were used in most cases and for each wavelength data were obtained for several pressures over a range of at least ten.

In order to interpret the absorption data, it is necessary to have some idea of the nature of the absorption spectrum, i.e., whether the absorption spectrum is a continuum, a diffuse band or a sharp band. For a continuum or a very diffuse band, high resolution is not required and, as a rule, Beer's law holds at relatively low pressures. On the other hand, the resolution we have used was not sufficient to give accurate k-values for sharp bands and the data showed an apparent pressure effect. Absorption laws have been reviewed, for example, by Nielsen, Thornton and Dale (1944).

Figure 4 represents a recorder trace of a partially resolved spectrum of the Schumann-Runge bands. The curve designated I_0 represents a portion of the hydrogen continuum. It can be seen that the resolution was not adequate to resolve the P and R branches of the rotational structure. For this type of band, the apparent k-values varied with pressure. Nevertheless, these values give some idea of the magnitude of absorption intensity and may be useful for semi-quantitative applications and for detection of intensity anomalies in a band progression. In the following discussions, regions of various spectra where the data are semi-quantitative will be pointed out.

Purification of gases and other items pertaining to a particular gas will be described in conjunction with the result and discussion of the gas.

3. OXYGEN

Absorption coefficients of oxygen have been measured more extensively than those of any other gas (see Section 1). However, to make the data more complete it would be desirable (a) to obtain values in the region from 1670 to 1900 Å; (b) to fill a number of gaps in the shorter wavelength regions; and (c) to establish the value at Lyman alpha.

The oxygen sample (Linde Air Company) used in this measurement required no purification. Mass-spectrometric analysis showed about 0.1 percent impurity, but this was mostly nitrogen which is quite transparent in the region of investigation. Pressures from 0.1 to 500 mm Hg were used.

For convenience c discussion, the results are divided into three spectral regions: the first region extends from about 1900 Å to the convergence limit of the Schumann-Runge bands which are vibrational bands superimposed on what appears to be a continuun; the second covers the Schumann-Runge dissociation continuum; and the third includes a number of diffuse and sharp bands separated by rather transparent windows. Papers on the absorption spectrum of oxygen in these regions by Price and Collins (1935), Knauss and Ballard (1935), Hopfield (1946) and Tanaka (1952) have provided helpful information as to some of the details of the spectrum which were not resolved by our equipment. Figure 5 represents the potential energy curves of the well-known electronic states of molecular oxygen.

ev

10

8

6

4

2

E

$B^3\Sigma_u^-$

$\overline{O^1D}\ \overline{O^3P}$

$A^3\Sigma_u^+$

$\overline{O^3P}\ \overline{O^3P}$

$\underline{O^1S}\ \underline{O^3P}$

$\overline{O^1D}\ \overline{O^3P}$

$b^1\Sigma_g^+$

$a^1\Delta_g$

O_2

$X^3\Sigma_g^-$

r →

$B^3\Sigma_u^-$

$A^3\Sigma_u^+$

"Herzberg"

"Schuman-Runge"

$b^1\Sigma_g^+$

$a^1\Delta_g$

$X^3\Sigma_g^-$
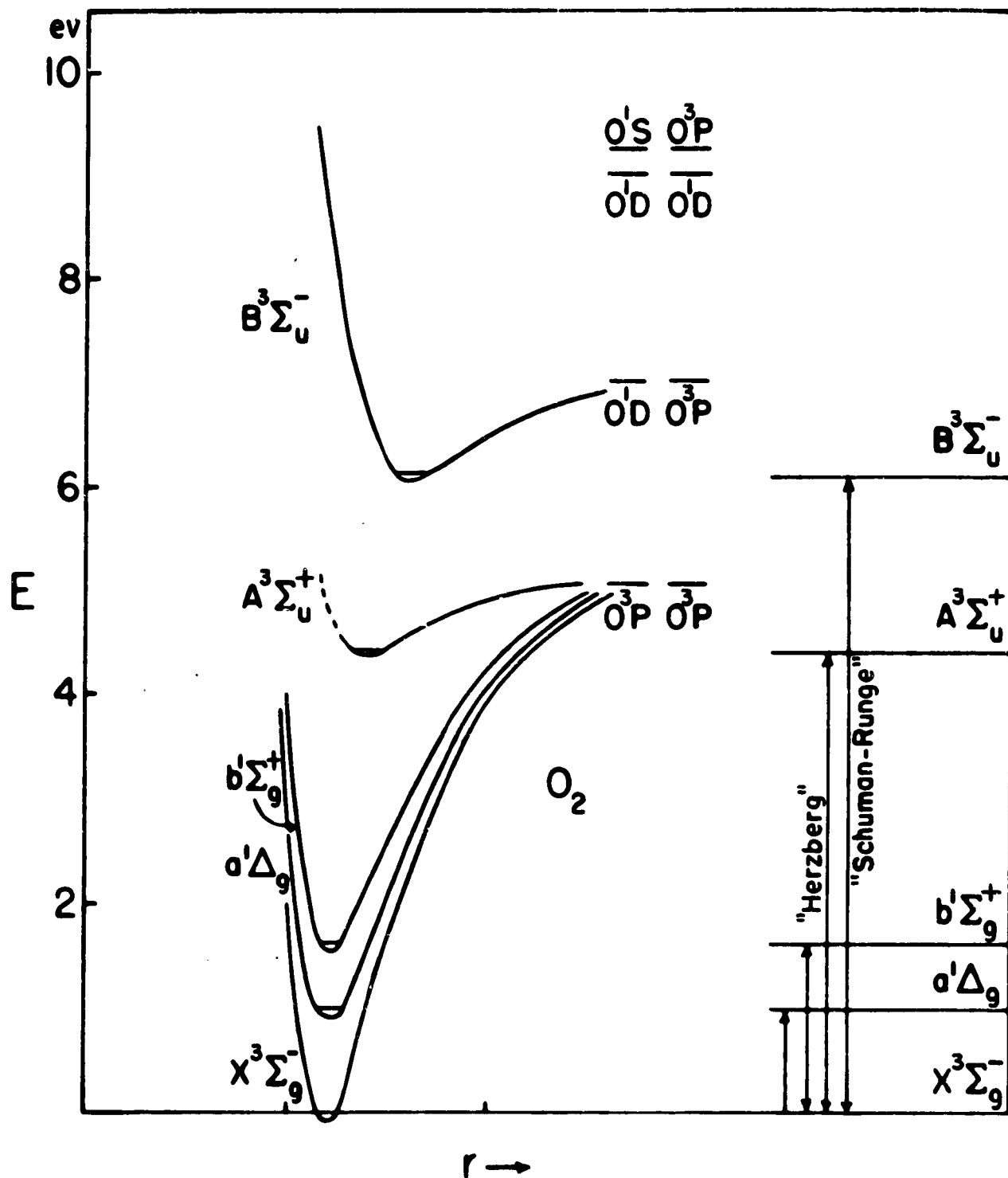
Fig. 5. Potential energy curves of molecular oxygen.
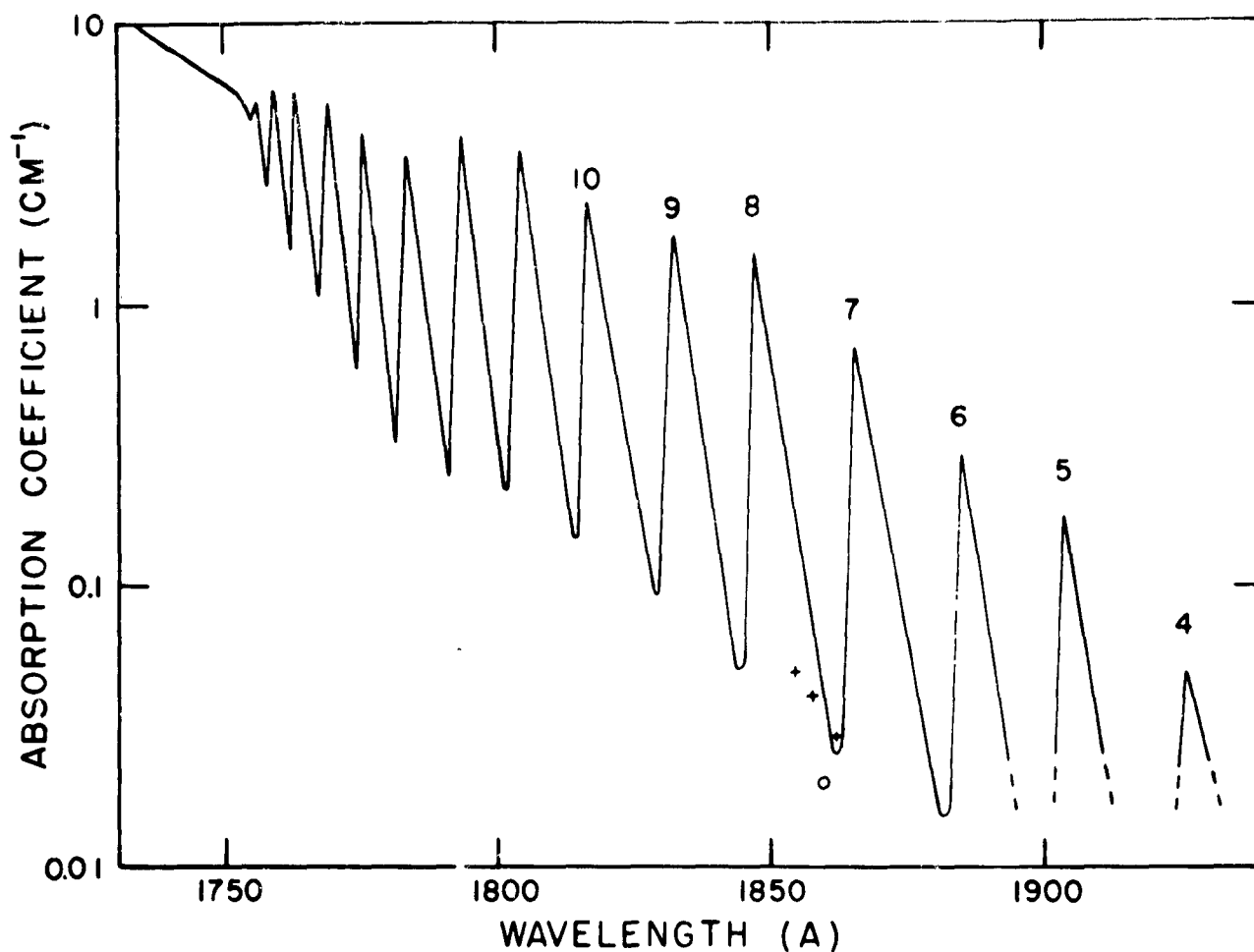
Fig. 6. Absorption intensities of the Schumann-Runge bands.

The absorption intensities of the Schumann-Runge bands have been calculated theoretically by Pillow (1950). In Table 2, these are compared with the results of this work. For the experimental data, the absorption intensities are relative values with that of the 12,0 band arbitrarily taken as 100. The oxygen pressure was 7.8 mm Hg and this pressure was too low for observation of bands below 8,0.

Table 2. Intensities of the Schumann-Runge bands.

Band	5,0	6,0	7,0	8,0	9,0	10,0	11,0	12,0	13,0	14,0	15,0	16,0	17,0	18,0
Theoretical......	1	5	20	29	51	50	78	100	90	95				
Experimental....				39	42	59	90	100	87	124	146	161	166	160

Considering the type of data being compared, the agreement is rather good; however, data obtained at higher pressures show that the decrease of intensity is less rapid from 6,0 to 4,0 than the evaluation by Pillow.

3.2. RESULTS FOR THE SPECTRAL REGION FROM 1750 TO 1300 Å

For the Schumann-Runge dissociation continuum $^3\Sigma_u^- \rightarrow {}^3\Sigma_g^-$, the important absorption measurement of Ladenburg and van Voorhis (1933) has been generally accepted and applied to atmospheric absorption. Their result showed a maximum absorption (k about 490 cm^{-1}) at 1450 Å with a nearly symmetrical intensity distribution. This is consistent with the dispersion measurement made earlier by Ladenburg and Wolfsohn (1932). The index of refraction of oxygen, obtained experimentally, was expressed by three resonance wavelengths and one of them ($\lambda_2 = 1468$ Å) was ascribed to the Schumann-Runge continuum. Still earlier, Koch (1912) had obtained a dispersion equation with $\lambda_2 = 1421$ Å.

By varying the pressure over a wider range (0.1 to 50 mm), it was possible to extend the work of Ladenburg and van Voorhis to both longer and shorter wavelengths, and the result is shown in Fig. 7 by the solid curve which represents the mean of several hundred points. Within experimental error (about 5 percent), Beer's law held over a pressure range of a factor of 20. The result of Ladenburg and van Voorhis is shown by the dashed curve which is considerably higher over the major part of this region. The maximum in the present observation is rather flat and is 380 cm^{-1} at about 1420 Å (this wavelength agreeing with the value given by Koch). The intensity distribution is rather asymmetric, the short wavelength side being fairly steep, and there may be a discontinuity at about 1400 Å due to an interaction of potential curves ($B^3\Sigma_u^-$ and an as yet unidentified curve). Although Steuckelberg (1932) obtained theoretically an intensity distribution curve agreeing fairly well with the data of Ladenburg and van Voorhis, it must be recalled that his calculation depended partly on their experimental data.

Since the discrepancy shown in Fig. 7 appears to exceed the combined experimental error, a further check was desirable and was kindly provided by Jones, Taylor and Greenshields (1952). Using a Baird monochromator, but an RCA quartz photomultiplier, they measured down to the limit of quartz transmission, and our result agrees with theirs at least in the region from 1750 to 1570 Å (the lower wavelength being their limit). The following explanation might be made regarding the photometry used by Ladenburg and van Voorhis. It is reasonable to suppose that the fixed sector disks used by them for intensity calibration reduced the sizable amount of scattered light, as well as the intensity of desired wavelengths. In this case, the calibration data may not be directly applicable to lines which have been greatly reduced in intensity because of the absorption of O_2, since O_2 itself would probably not have reduced the amount of scattered light, at least not so much as did the sector disk. This argument is based on the "fact" that scattered light in a spectrograph consists mostly of wavelengths longer than 2000 Å.

Three minor maxima at 1293, 1332 and 1352 Å were observed on the short wavelength slope of the continuum. These were recently found photographically by Tanaka (1952) who used a Lyman continuum as source and varied the pressure of O_2. These bands or continua apparently escaped photographic detection for many years, since they are superposed on the slope of the strong continuum. Actually, by looking for them one can see them in a published photograph by Hopfield (1946). They were readily observed with the phosphor-coated photomultiplier, even using the many-lined spectrum of H$_2$ as source. According to Tanaka, these bands appear as continua with a 3-m grazing-incidence spectrograph and the wavelengths of the maxima could not be measured precisely. He has suggested that the first "continuum" at 1293 Å leads to the dissociation products $^3P + {}^1S$ and the other two to $^1D + {}^1D$ or $^3P + {}^1S$ (see Fig. 5).

Using Eq. (1), the f-value of 0.161 was obtained for the Schumann-Runge continuum (1290 to 1750 Å). This value is somewhat smaller than the value (0.193) obtained by Ladenburg and van Voorhis.
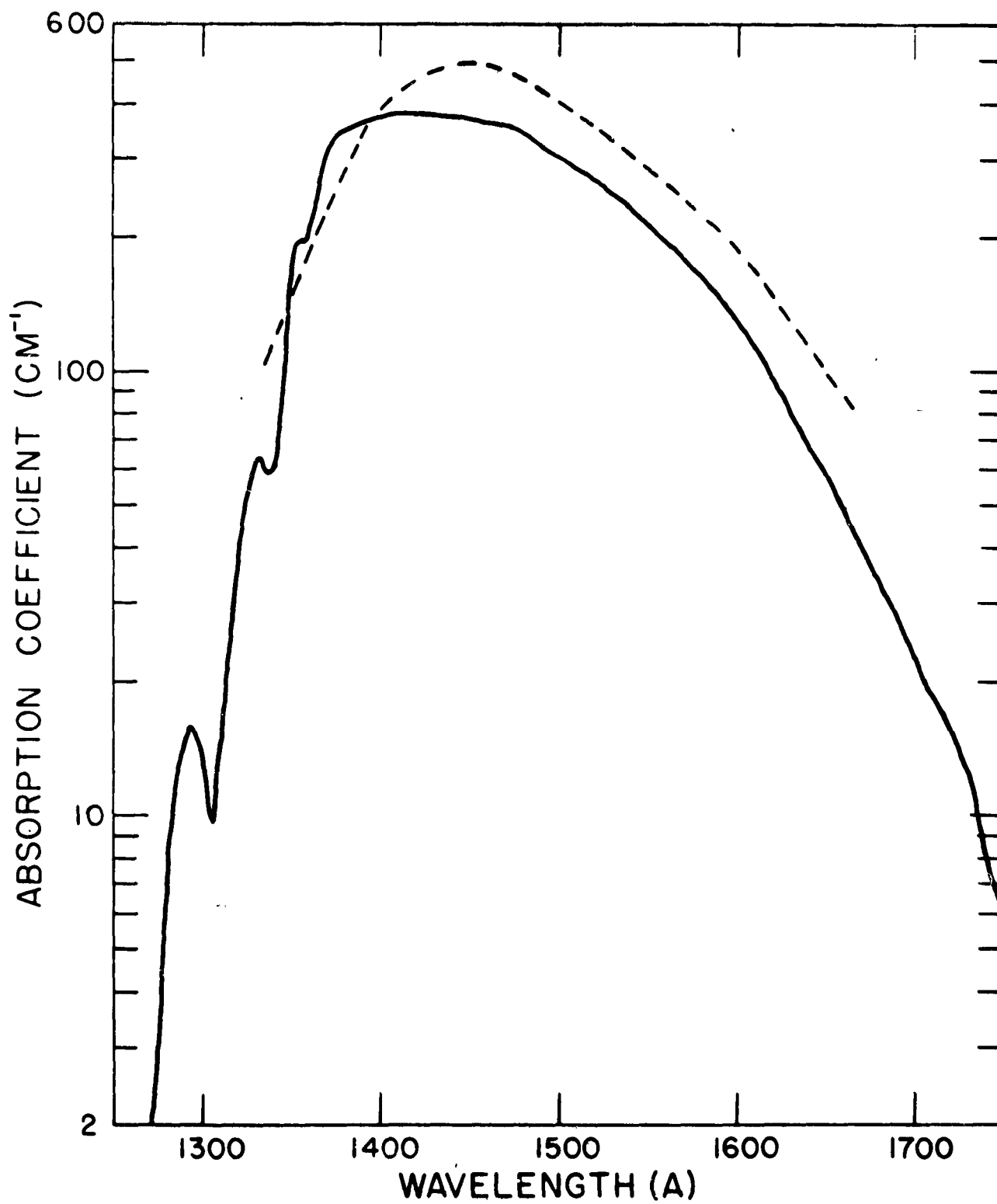
Fig. 7. The k-values of O_3 in the region from 1250 to 1750 Å.
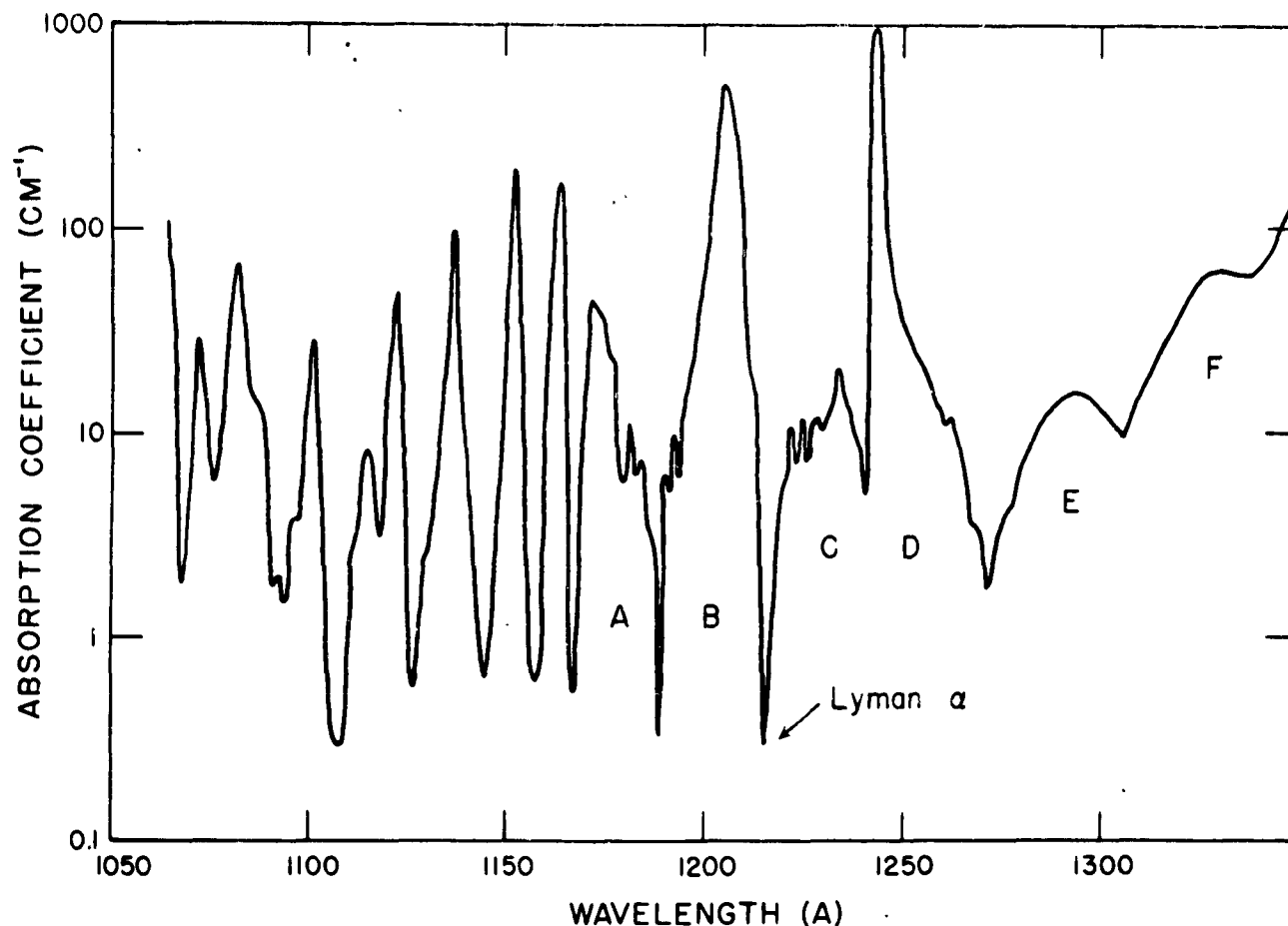
Fig. 8. The k-values of O_2 in the region from 1050 to 1350 Å.

3.3. RESULTS FOR THE SPECTRAL REGION FROM 1300 TO 1050 Å

Molecular oxygen has a complex absorption spectrum in this region and most of the bands still need to be classified. This region is of great importance to the study of the upper atmosphere, since solar radiation can penetrate down to the D layer through the several windows of the O_2 spectrum. For example, Lyman alpha lies in one of the deepest windows and its enhancement during chromospheric eruption may very well provide the necessary energy to account for the increased ionization and radio fadeout. Furthermore, it is important to know whether dissociation of O_2 by photons in this region of the spectrum supplies an appreciable amount of metastable oxygen atoms.

At Lyman alpha the absorption coefficient was found to be 0.30 cm^{-1} at pressures of 70 mm Hg and 0.50 cm^{-1} at 490 mm. These values are in close agreement with the data obtained by Preston (1940) who used pressures from 30 to 290 mm and a cell length of 21.8 cm. Since he observed a pressure effect, he extrapolated his data to zero pressure and obtained $k = 0.28$ cm^{-1}. Our extrapolated value was 0.27 cm^{-1}. Incidentally, absorption coefficients obtained by the present method for N_2, CO_2 and H_2O at Lyman alpha agreed remarkably well with those obtained by Preston.

Because of the complexity of the O_2 spectrum and the fact that a many-lined spectrum rather than a continuum was used as source, some of the data in this region are not reliable. In the region below 1170 Å

the absorption bands show sharp, fine structure as well as some diffuseness. The "coefficient" shown in Fig. 8 for the poorly resolved region from 1060 to 1170 Å must therefore be considered semi-quantitative. As in the case of the Schumann-Runge bands, the maxima are probably too low and the minima too high, although the apparent pressure effect was somewhat less. Included in the paper by Weissler and Lee (1952) are k-values at 7 wavelengths in this region. These are, in general, considerably larger, and may be explained by the fact that they used higher resolution. Although close comparison may not be justified, Schneider's values (1940) for this region seem to be, in a rough way, lower than those obtained by Weissler and Lee.

In Fig. 8, the bands A, B, C, D, E and F are very diffuse with hardly any structure, even when observed with a 3-m grazing-incidence spectrograph. Price and Collins (1935) who observed most of them ascribed the diffuseness to predissociation. This was confirmed by Tanaka (1952), who studied the spectrum in greater detail. The latter also reported two new progressions, one of which was suggested to be a member of the Rydberg series converging to the first ionization potential. A few members of these progressions seem to appear in our data (Fig. 8). Because of the general diffuseness of the spectrum, the k-values shown in Fig. 8 for the region from 1170 to 1300 Å should be fairly reliable.

Price and Collins (1935) also observed a weak continuum at 1105 Å, extending toward shorter wavelengths. The present measurements support their observation; however, its intensity (about 2 cm^{-1} in Fig. 5) is much less than the estimate (50 to 100 cm^{-1}) reported by Weissler and Lee (1952).

4. OZONE *

Many investigators have studied the ozone molecule by optical methods to determine its molecular structure and to obtain quantitative data on its absorption spectrum, particularly in connection with the study of atmospheric ozone. As a result, a number of bands and continua have been found in the ultraviolet, visible and infrared regions, and although ozone is somewhat unstable, a sizable amount of reliable data on absorption coefficients and effects of temperature and pressure is now available. These, however, will not be reviewed here.

In the vacuum ultraviolet region, the only experimental investigation appears to be that made by Price and Simpson (1941). According to them the result was "disappointing," since the photographic plates showed no strong absorption bands in the region from 2300 to 1600 Å. In the region below 1600 Å a strong continuum appears in the reproduction of their photographic plate. They stated, however, that in this region the absorption of O_2 resulting from the photodissociation of ozone prevents further investigation.

To determine the absorption spectrum and the k-values of ozone in the vacuum ultraviolet, it is necessary to use very pure ozone. Since ozone decomposes readily and is chemically reactive, it is almost impossible to obtain pure ozone. If the amount of impurity is small, however, corrections may be made by using the absorption coefficients of the gases appearing as impurities. In this way, it was possible to obtain absorption coefficients of ozone from 2200 to 1050 Å.

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* This work was done in collaboration with Dr. Y. Tanaka. His extension of the work to longer wavelengths will be reported separately by him.
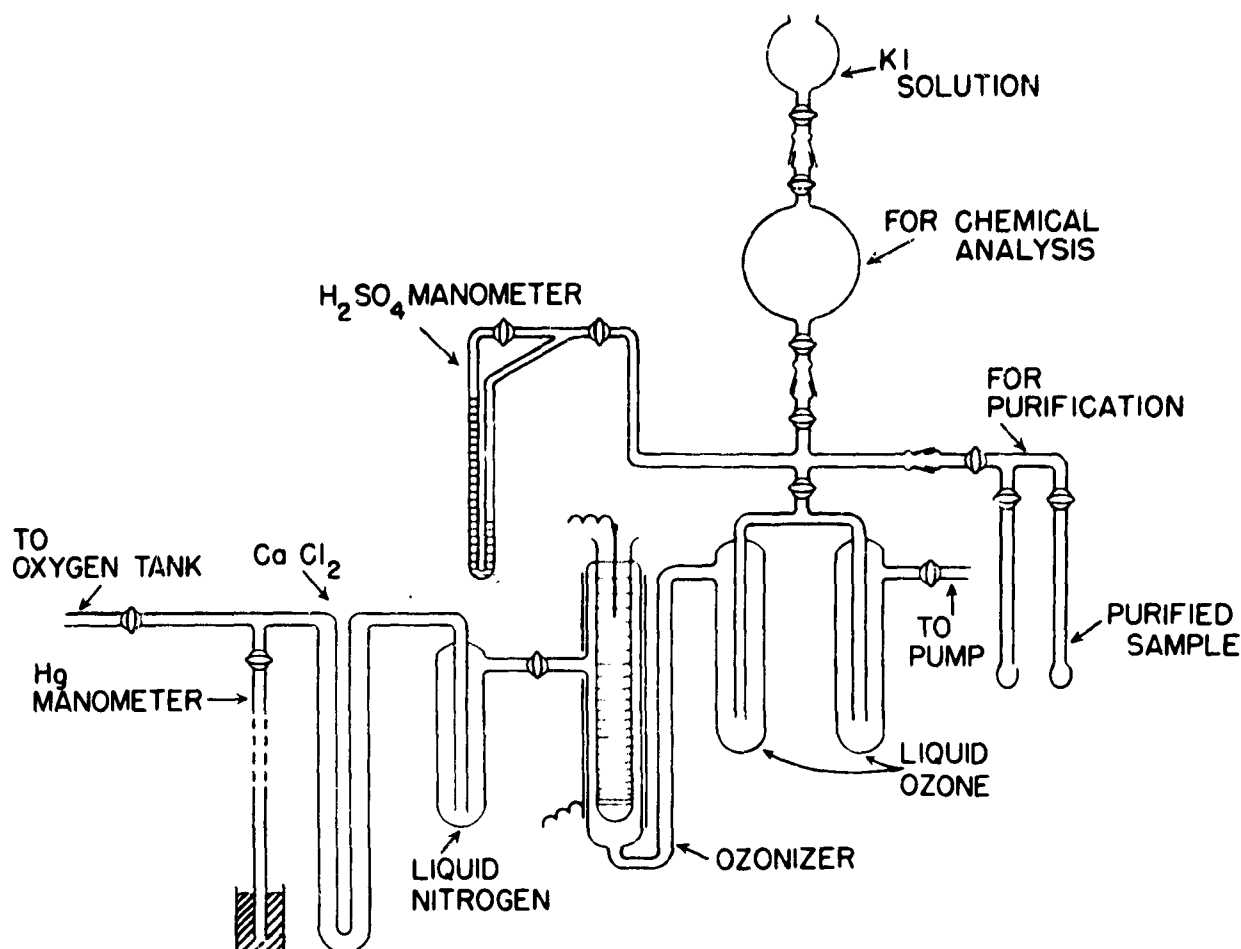
Fig. 9. Preparation and purification system for liquid ozone.

4.1. PREPARATION OF OZONE AND CONDITIONS OF ABSORPTION MEASUREMENT

Figure 9 shows schematically the apparatus used in the preparation and purification of ozone. Tank oxygen was passed through a long $CaCl_2$ drying tube and then through a liquid nitrogen trap, thus removing H_2O and CO_2 which might be present as impurities. The oxygen was then passed into the ozonizer, consisting of a double-wall pyrex tube, the inside of which was filled with aqueous NaCl and the outer wall wrapped in thin aluminum foil. A 15-kv, 450-va transformer was used for the excitation. Liquid ozone was collected in liquid nitrogen traps. Since oxygen is the main impurity, the gas pressure in the ozonizer was kept below 12 cm Hg to prevent condensation of oxygen, together with ozone. After collecting a few cc of liquid, the process was stopped and the system pumped for about half an hour, until the pressure decreased to about 0.1 mm Hg (the vapor pressure of O_2 at liquid O_2 temperature). (See Jenkins and Birdsall (1952).)

If nitrogen is present in tank oxygen, the ozonizer would produce nitrogen oxides that would condense with ozone. Since these oxides have strong absorption in the Schumann region, their presence could not be tolerated. Accordingly, the ozone samples chosen for study were obtained by several fractional distillations of the liquid, retaining only the middle portion each time.

To fill the absorption cell, liquid ozone was transferred to the gas-filling system. The transfer was accomplished without any explosions by keeping the ozone cooled in liquid nitrogen until just prior to the absorption measurements. The liquid was allowed to evaporate slowly into the cell and the pressure measured with a U-type H_2SO_4 manometer. For pressure measurements below 1 mm Hg, an expansion method was used. The vapor pressure of H_2SO_4 at room temperature did not produce any noticeable absorption as was shown by a blank run. Since ozone decomposes at an appreciable rate, the duration of each run was limited to five minutes, during which time a range of 100 Å could be covered. For each wavelength region, four or five different pressures were used. Pressures from 0.2 to 25 mm Hg in the absorption cell were used to cover the absorption intensities.

During the filling of the absorption cell (previously evacuated to $\sim 10^{-5}$ mm Hg) an interesting phenomenon was observed. As the liquid ozone evaporated into the cell, a sudden increase in photomultiplier current, reaching a maximum value in a few seconds, was observed. The current then decayed to its original value. Upon pumping out the ozone, the photomultiplier current again increased and decreased, although, in this case, the rate of current change was slower and the maximum was much less. This phenomenon occurred both with the light source on and off, and may be due to chemiluminescence on the inside of the cell. No doubt some ozone decomposed in this process, giving rise to oxygen impurity, but the amount was small as determined subsequently from the absorption data.

4.2. DETERMINATION OF PURITY

The purity of the ozone sample was determined by a combination of three methods. First, the vaporized ozone was allowed to react with aqueous KI and the liberated I_2 titrated with standard $Na_2S_2O_3$. Here the ozone was found to be 90 to 95 percent pure for all samples taken from the purification system and from the gas-filling system. To determine the amount of nitrogen oxides, a Consolidated Engineering Corporation analytical mass spectrometer was used. The analysis showed no detectable amount of nitrogen oxides in the ozone sample, indicating that the nitrogen oxide content was less than 0.05 percent. For this analysis, the sample was allowed to stand several days to convert the ozone to oxygen, since ozone may attack the metal parts of the mass spectrometer. Under this condition, the analysis for CO, CO_2, H_2O and hydrocarbons would result in high values, because their formation by the action of ozone on stopcock grease would be exaggerated by the length of the exposure time. Therefore, an analysis of these gases was not made. The absorption measurement itself served as the third method for estimating the amount of impurities. This was made possible by the data for a number of gases obtained previously with the same absorption apparatus. There are three strong peaks for CO_2, at 1088, 1119 and 1129 Å, with k-values of 3600, 4400 and 2500 cm^{-1}, respectively, and these appeared on the uncorrected absorption curve of O_3. The data showed that the amount of CO_2 was between 1 and 2 percent. Similarly, from a strong oxygen peak ($k = 940$ cm^{-1}) at 1243 Å, the amount of O_2 in the absorption cell was found to be about 7 percent. The presence of CO was indicated by five weak but sharp peaks which corresponded to the heads of the CO Fourth Positive bands from (0,0) to (4,0). The amount of CO was estimated to be a few percent.

Although the chemical method showed that the total amount of impurities was less than 10 percent, the absorption data indicated that the value was somewhat higher, at least in the absorption cell. This is quite possible, since the reaction described above can provide the additional impurities. In general, the absorption data showed that when relatively high ozone pressures were used, the percentage of impurity
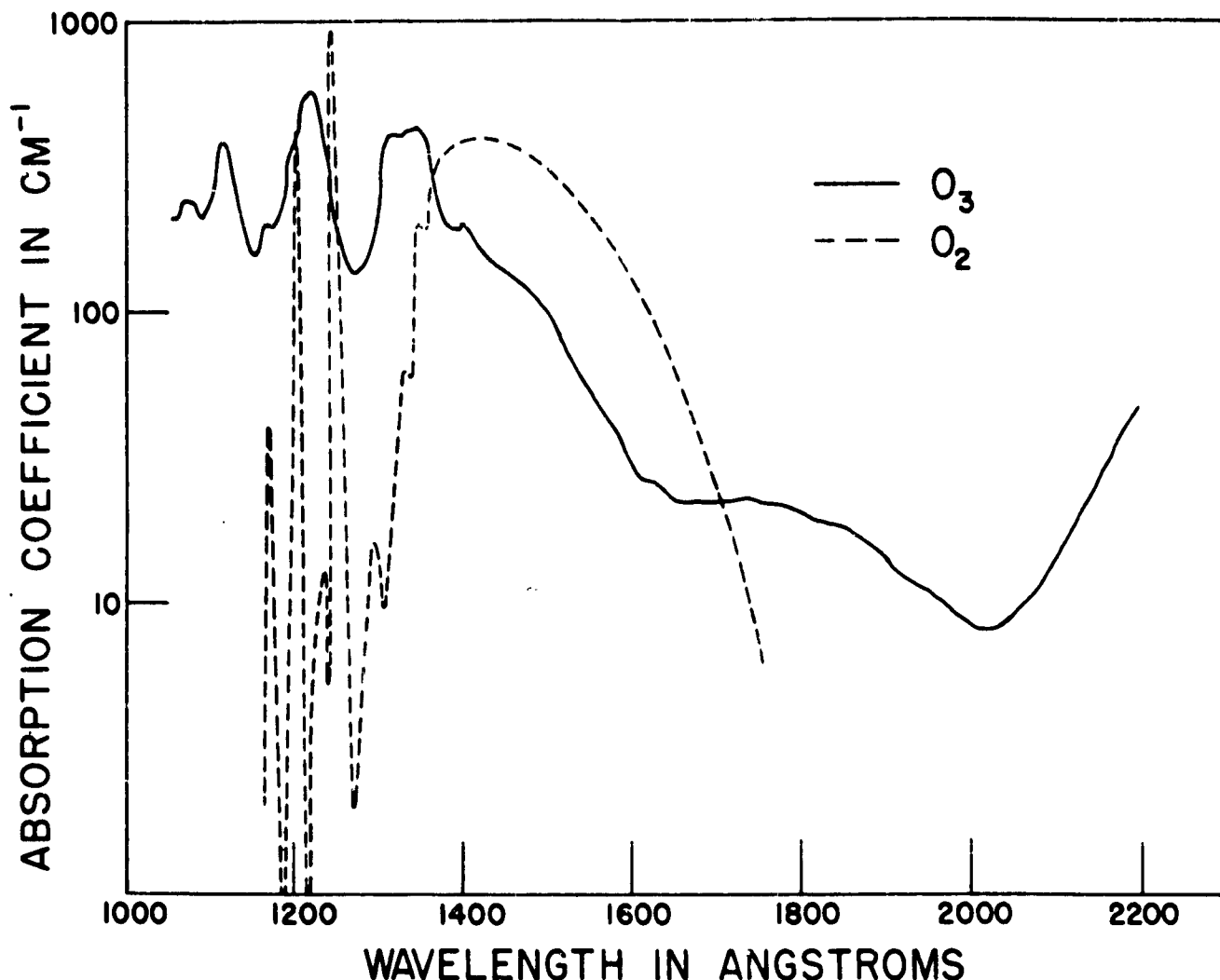
Fig. 10. The k-values of O_3 in the region from 1050 to 2200 Å.

was low,more nearly agreeing with the chemical determination. Therefore, to obtain the corrected absorption intensity curve for ozone, only the data obtained with the highest pressures were used. In view of all these uncertainties, it is estimated that the combined experimental error would be as high as 10 percent.

4.3. RESULTS AND DISCUSSIONS

The solid curve in Fig. 10 represents the absorption curve of O_3. This curve was obtained after corrections for O_3, CO and CO_2 were applied to the original data. It cannot be an absorption curve of an unknown impurity with very high absorption coefficients (order of 10^4 cm^{-1}), since the result was reproducible in spite of the fact that the various observed impurities varied considerably for different runs. The absorption curve (dashed) for O_2, the main impurity, is included for comparison.
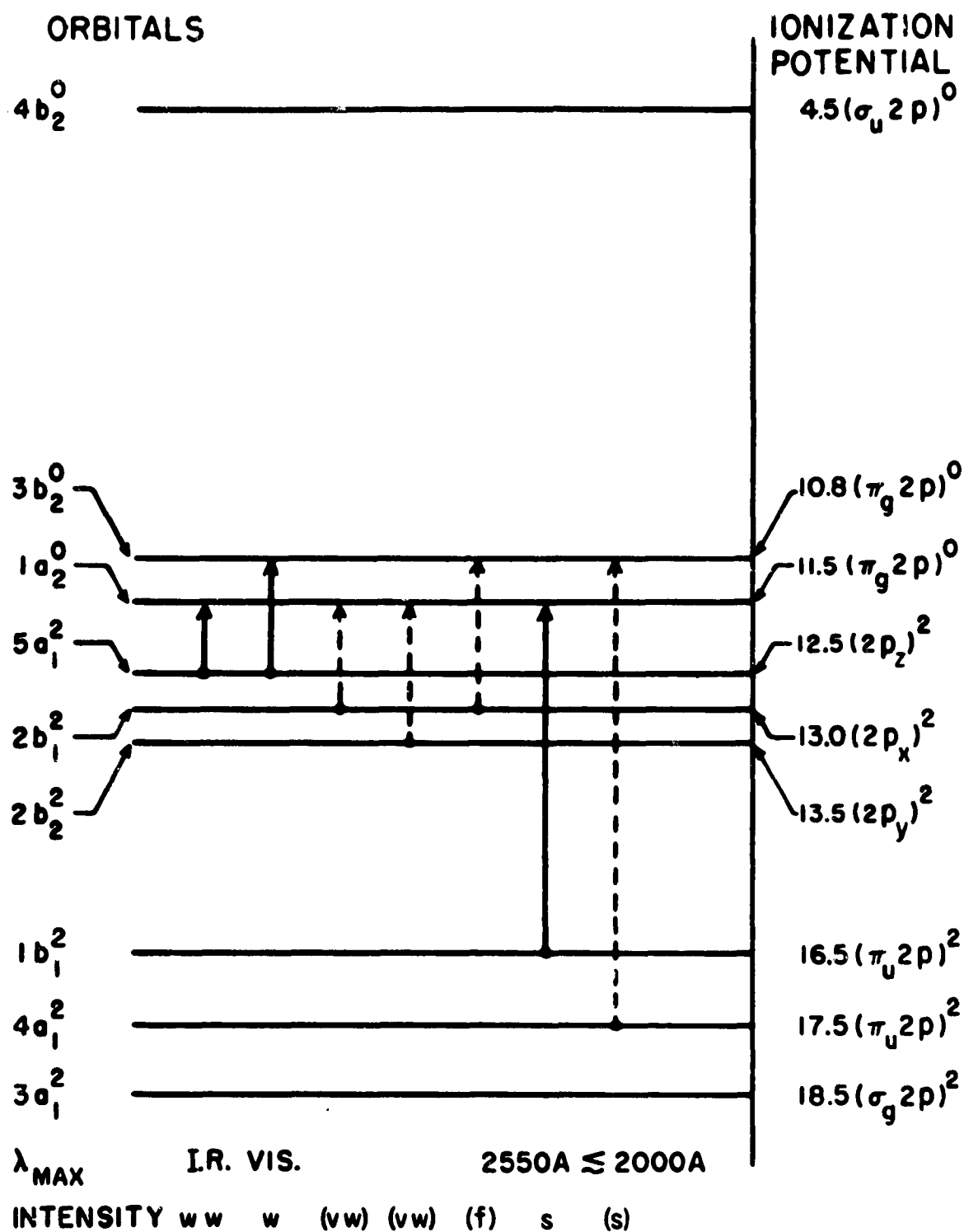
Fig. 11. Predicted and observed electronic transitions for O_3.

For convenience of discussion, the regions above and below about 1300 Å will be considered separately. Above 1300 Å there appear to be continua with maxima at 1725, 1450 and 1330 Å. The 1725 Å continuum merges at about 2000 Å with the known, strong continuum which has a maximum at 2550 Å. The region from 2020 to 2200 Å, shown in Fig. 10, overlaps the region studied by Ny Tsi-Ze and Choong Shin Piaw (1933) and by Vassy (1941), who measured down to 2135 and 2020 Å, respectively. The values in this region were found to be somewhat smaller than their values. The difference was about 10 percent at 2200 Å and about 40 percent at 2020 Å as compared to the data reported by Vassy. The discrepancy at about 2020 Å appears to be greater than the combined experimental error. It is difficult to assess the errors since the experimental conditions are quite different: the use of ozonized oxygen, photographic photometry, quartz spectograph, and absorption cell placed before the entrance slit against the use of purer ozone, linear photoelectric photometry, vacuum monochromator, and absorption cell at the exit slit. It is possible that too small a correction was applied to the present data and this may account for about 10 percent. A further investigation seems desirable.

Mulliken (1942) has proposed an electronic configuration for ozone and Fig. 11 shows schematically his results, all notations being his, where the solid arrows indicate observed transitions and dashed arrows indicate other predicted transitions. The strong band, $4a_1{}^2 - 3b_2{}^0$, predicted in the region just below 2000 Å was not observed in the present study. The 1725 Å continuum seems to correspond energetically with it but is much weaker than predicted. Moreover, our results agree with those of Price and Simpson (1941) who reported no bands in the region from 2300 to 1600 Å. Our absorption coefficient at 1600 Å is 35 cm^{-1}, gradually decreasing to a minimum at about 2000 Å. Energetically, the $3a_1{}^2 - 3b_2{}^0$ and $5a_1{}^2 - 4b_2{}^0$ transitions correspond very roughly to the observed 1725 and 1450 Å continua, respectively, although the transition probabilities are not known. It might also be noted that the three strong continua at 1120, 1215 and 1330 Å correspond fairly well to the energy differences among the orbitals $3a_1{}^2$, $4a_1{}^2$ and $1b_1{}^2$.

An element of uncertainty is introduced into these theoretical considerations since Mulliken adopted an acute apex angle (39°) for O_3. Recent infrared study by Sutherland and Penny (1936) and electron-diffraction measurement by Shand and Spurr (1943) seem to support an obtuse apex angle (127°). Without taking account of intensity relationships, the following transitions for the case of obtuse apex angle appear to correspond energetically with the observed continua.

Continuum Maximum		Attempted Transition
1725		$3a_1 \rightarrow 2b_1$
1450		$2b_2 \rightarrow 5a_1$
1330		$2b_2 \rightarrow 5a_1$
1215		$1a_2 \rightarrow 4b_2$
	or	$1b_1 \rightarrow 5a_1$

Figure 12 presents the ozone absorption spectrum for the region from 1300 to 1060 Å showing more details. Because of the weakness of the bands as compared to the continuum, it is difficult to determine progressions. However, there may be some progressions that have separations of ~600 and ~800 cm^{-1}. The continua having maxima at 1215 and 1120 Å are similar in shape and intensity to that at 1330 Å. It is possible that there are two other continua at 1165 and 1070 Å but the former does not have a prominent peak and the latter approaches the transparency limit of the LiF window, making it difficult to classify with certainty.
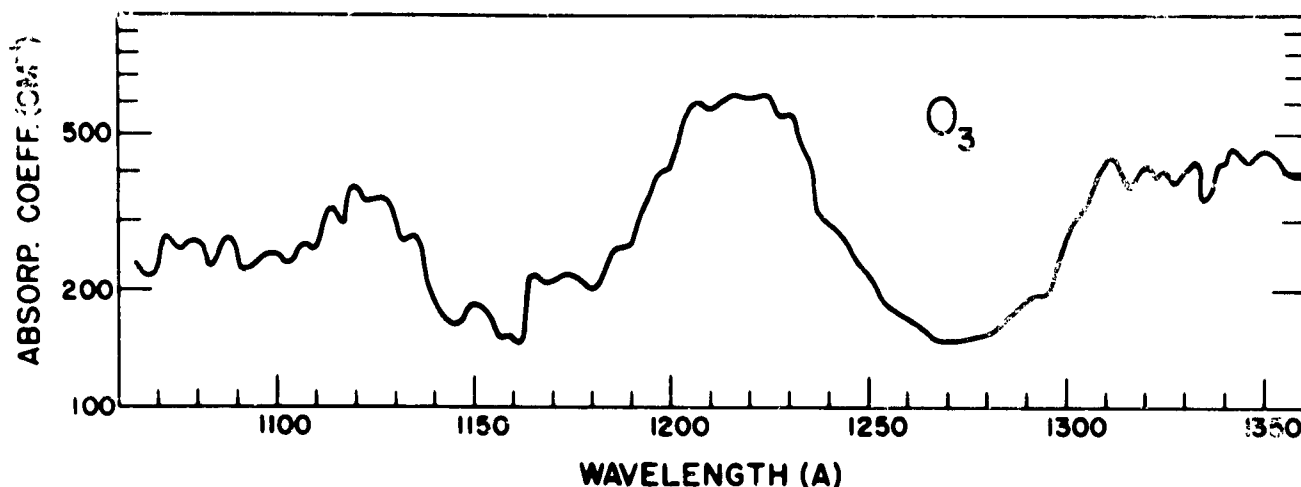
Fig. 12. Absorption curve of O₃ showing bands.

It is interesting to note that ozone has a high absorption coefficient at Lyman alpha where most of the gases reported present in the upper atmosphere have comparatively low coefficients, oxygen and nitrogen in particular. Water vapor is an exception to this with a k-value of 387 cm⁻¹. In the region of the Schumann-Runge continuum, the absorption intensity of ozone is almost as strong as that of oxygen. Furthermore, the intensity of the S-R continuum decreases rapidly on the long wavelength side, whereas, for ozone the decrease is very gradual. The absorption curves cross at about 1700 Å ($k = 20$ cm⁻¹).

It is apparent from the preceding discussion that further investigations are required to determine the electronic states of the ozone molecule. It is also desirable to measure the ionization potential, since Wulf and Deming (1938) have suggested that the D layer might be produced by the photoionization of ozone.

5. NITRIC OXIDE *

The presence of nitric oxide in the high atmosphere is not yet established. Laboratory experiments do show that this gas can be produced photochemically from N₂O, a known atmospheric gas, but the chemical process is not known with certainty. The formation of NO by other processes, such as the association of atomic oxygen and atomic nitrogen, have been proposed; however, quantitative data are extremely meager. Nevertheless, it is probable that NO is present in the atmosphere, and its importance would depend on its amount and distribution. In anticipation of the importance of NO, absorption data for this gas have been included.

The absorption spectrum of NO in the vacuum ultraviolet has been studied by Leifson (1926), Lambrey (1930), Tanaka (1949), Migeotte and Rosen (1950). Their data and those obtained from various emission spectra of NO have provided the basis for the electronic states of this molecule. These states are summarized in the energy diagram, Fig. 13. Although the dissociation energy is here shown as 6.48 ev, this value is still the subject of controversy as in the case of N₂.

* F. F. Marmo contributed a major part in this work. A more complete report will be published by him in *J. Opt. Soc. Amer.*

eV

12 —

NO$^+$

^4S_u ^1S_g 10.68 ev (1161A)

^2P_u ^3P_g 10.05 (1232A)

10 —

1st Ionization Potential (9.5ev) 1306A

^2D_u ^3P_g 8.87 ev (1397A)

E $^2\Sigma$

D $^2\Sigma$ 8.45 (1466A)

$^4\Sigma^-$

C $^2\Sigma$ 8 —

^4S_u ^1D_g

E $^2\Sigma$ 7.54 ev

$^2\Pi$

D $^2\Sigma$ 6.60

A $^2\Sigma^+$ ^4S_u ^3P_g 6.48 (1911A)

C $^2\Sigma$ 6.49

Frost Bands

$^2\Phi$

6 — B $^2\Pi$

B $^2\Pi$ 5.63

N O

A $^2\Sigma$ 5.47

$^4\Pi$

$1s^2 2s^2 2p^3$ $1s^2 2s^2 2p^4$

4 —

X $^2\Pi$

1878A

1915A

2200A

2264A

2 —

NO

ϵ

δ

β

γ

1.0   2.0 A

r ⟶
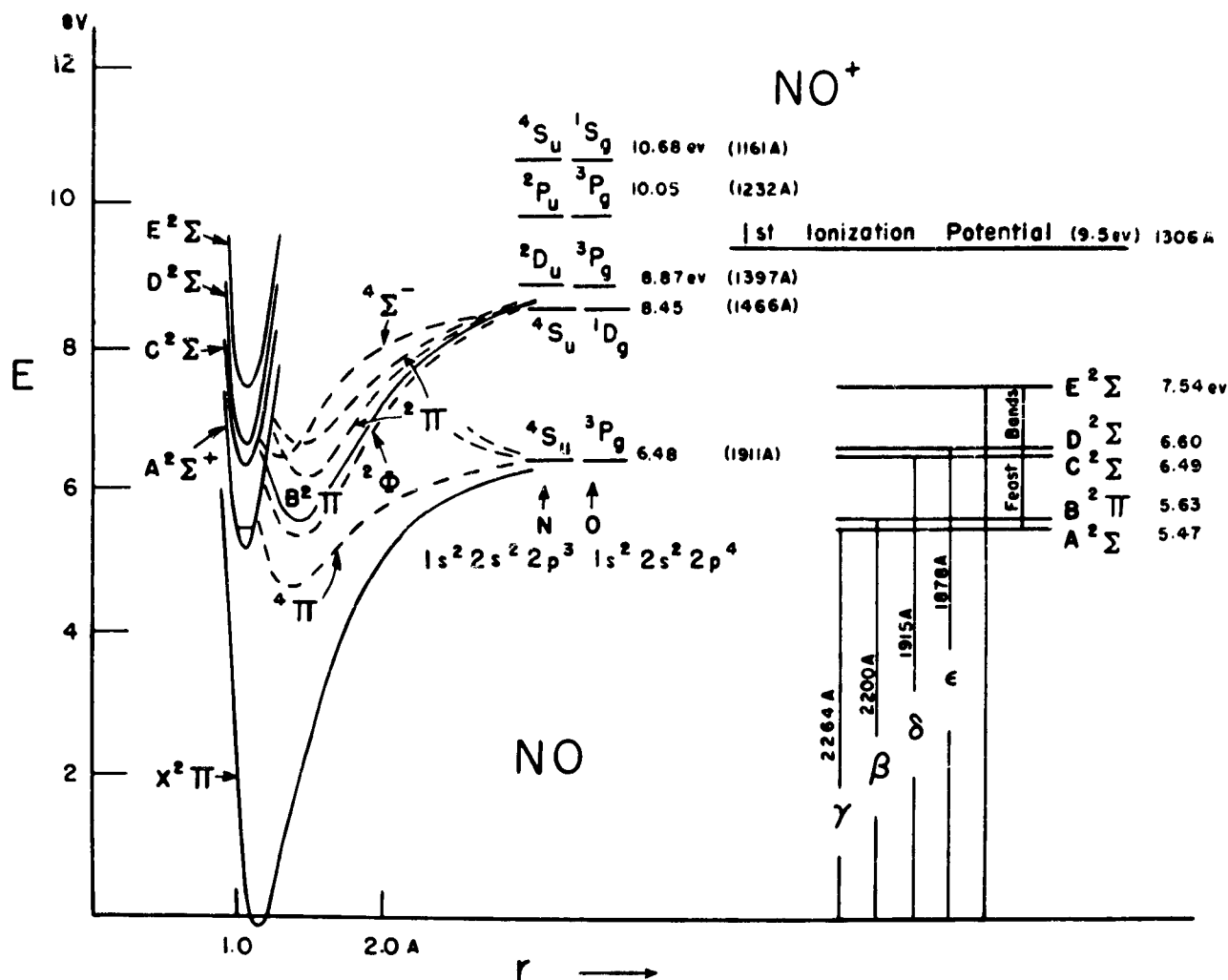
Fig. 13.   Potential energy curves of NO.

The ultraviolet absorption bands of NO which have been classified lie mainly in the region from 1500 to 2300 Å.   Very little is known at lower wavelengths besides the three Rydberg series observed by Tanaka (1942) in the region below 1000 Å.   The energy diagram of NO, however, suggests a number of possibilities in the region from 1000 to 1500 Å.   There are possibilities of dissociation continua as well as band spectra. Furthermore, the first ionization potential is 9.4 ±0.2 ev (or about 1320 Å) according to electron impact measurements by Hagstrum (1951) but no Rydberg series nor ionization continuum have been identified.

The only measurement of absorption coefficients of NO in the vacuum ultraviolet is that due to Mayence (1952).   She made photographic absorption measurements using a grating spectrograph down to about 1400 Å, and reported a weak continuum with a maximum at 1470 Å.   In the region below 1400 Å, there appear to be no published data on k-values.

5.1. PURIFICATION OF NO

In order to obtain reliable quantitative data for NO in the Schumann region, gas samples of high purity are required.   Most of the gases which are possible impurities, have rather high k-values in this region. As described below, it is not safe to assume the purity of this gas even after careful purification.
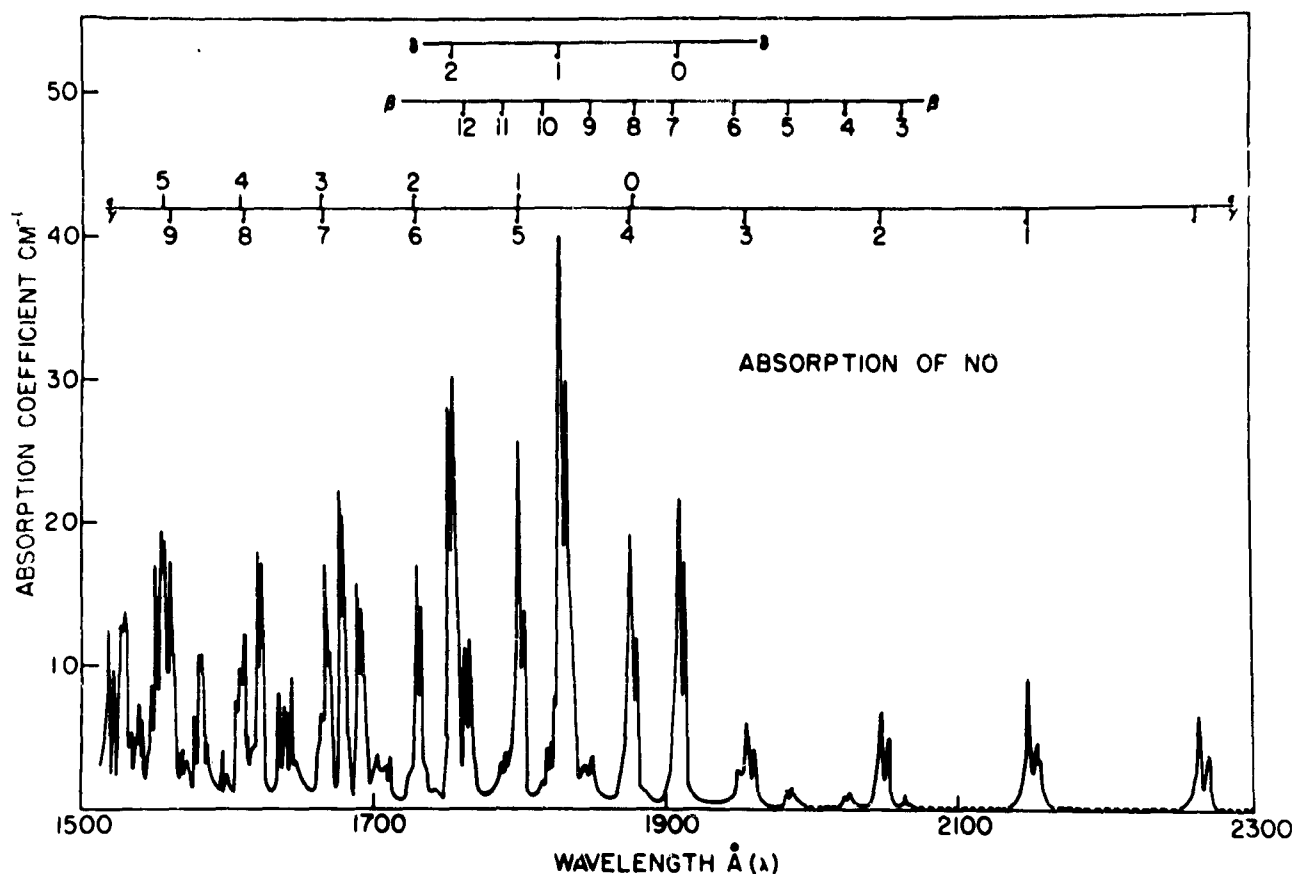
Fig. 14. Absorption curve of NO in the region from 1500 to 2300 Å.

Nitric oxide was purified from tank gas by a method similar to that used by Johnston and Giauque (1929). In spite of the fact that the first purified sample was carefully obtained, a mass spectrometric analysis revealed almost 3 percent of N_2O. Preliminary absorption data, however, were obtained with this sample. Then the first sample was subjected to repeated fractional distillation until the total impurity was less than 0.05 percent. The preliminary and the final absorption curves showed a conspicuous difference: the former had a definite maximum of continuous absorption at 1285 Å where the final curve appeared flat. In fact an application of the absorption coefficient of N_2O at this wavelength indicated 3 percent of N_2O, in agreement with the mass spectrometric analysis.

5.2. RESULTS FOR BAND SYSTEMS

The absorption spectrum of NO in the region from 1400 to 2300 Å consists of several systems of sharp bands which include the β, γ, δ and ϵ bands (see Figs. 13 and 14). There is very little overlapping of these bands above about 1900 Å. At lower wavelengths, however, the spectrum is very complex, with many overlapping bands and the classification of bands in the region from 1400 to 1700 Å is still rather incomplete.

The resolution (about 1 Å) used in the present experiment was not adequate to resolve the fine structure of the various bands and so the measured k-values are only semiquantitative. Fig. 14 represents the

ABSORPTION OF NO BANDS
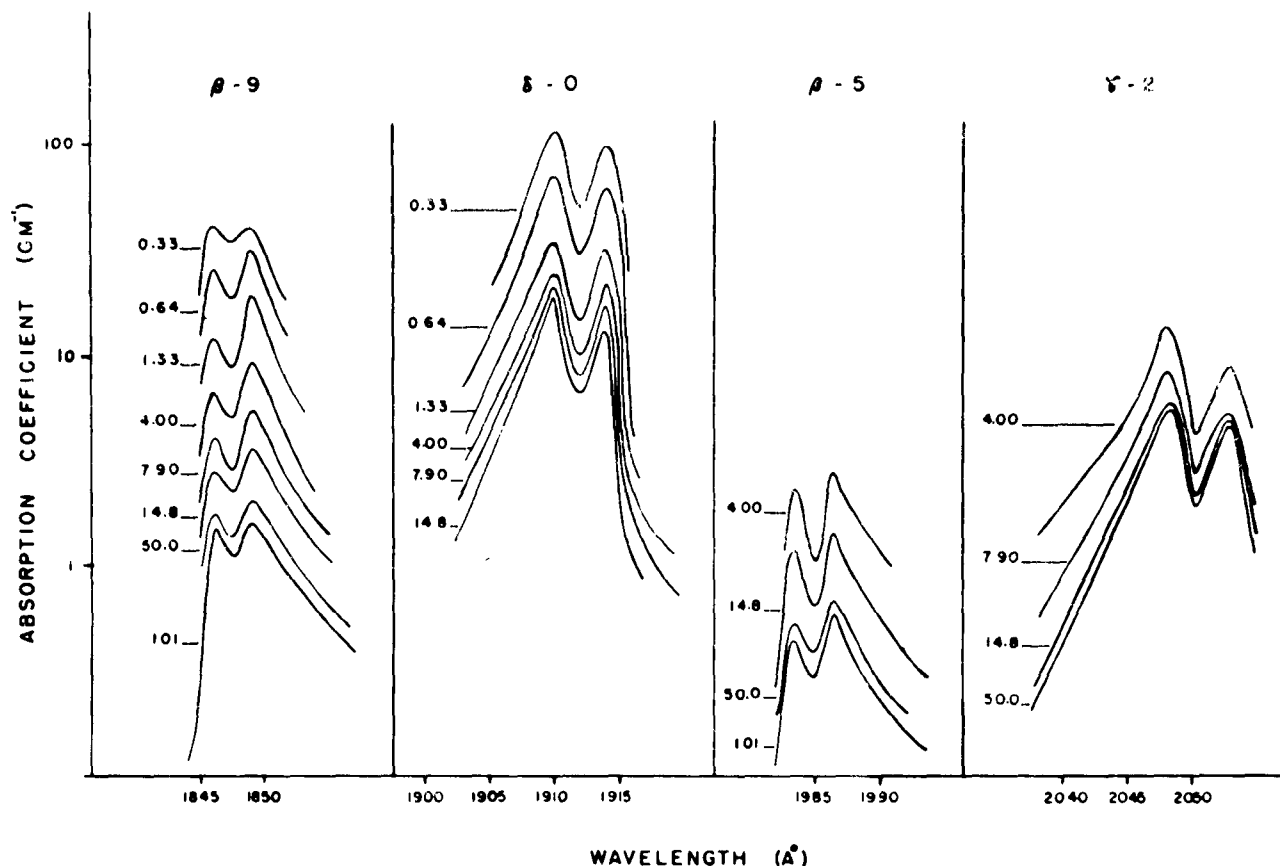
Fig. 15. Apparent pressure effect of NO bands.

apparent absorption intensity of the NO spectrum in the region from 1500 to 2300 Å obtained with a pressure of 14.8 mm Hg in the absorption cell (47 mm). The position of the β, γ, δ and ϵ bands are indicated at the top. As in the case of the Schumann-Runge bands of O_2, the measured k-values showed a strong, apparent pressure effect which might be attributed entirely to the lack of resolution, although a true pressure effect, particularly at high pressure, is not excluded. The apparent pressure effect is shown in Fig. 15 for four bands (β-9, δ-0, β-5, γ-2). The number adjacent to each curve is the pressure (in mm Hg) of NO which was varied from 0.33 to 101 mm to cover the absorption intensities in the region from 1500 to 2300 Å. All the observed bands in this region showed a similar effect: as the pressure is increased, the k-value decreases rapidly at first and then more slowly so that, in some cases, it even appears to approach a limit.

Mayence (1952), who used a spectrograph with about the same resolution, found that, for at least some of the β bands, the k-value was independent of pressure in spite of the lack of resolution. The pressure that was used, however, covered a comparatively narrow range (about a factor of 5), and the product of cell length and pressure was about one order of magnitude greater than the largest product used in the present work. For example, for a cell length of 500 mm, Mayence obtained the following k-values for the shorter wavelength peak of the β-5 band: 0.21 cm^{-1} for a pressure of 60 mm Hg and 0.17 cm^{-1} for a pressure of 200 mm. These values are not strictly constant and they appear to be consistent with the data for

the β-5 band shown in Fig. 15 which was obtained with a cell length of 47 mm. Thus, it is suggested that the conclusion made by Mayence might not be justified, at least for the lower pressures that she did not use. It may be added that Mayence found that k-values varied inversely as the square root of cell length for lengths from 1 to 500 mm.

As in the case of the Schumann-Runge bands, the k-values for the NO bands, although semiquantitative, may be applied to absorption measurements obtained with another optical system with equivalent resolution. This may be of importance in rocket spectroscopy to determine the amount of atmospheric NO. Furthermore, the absorption data may be useful for measurements of relative absorption intensities within a given band system.

The relative intensity distribution of the γ bands was found to be in good agreement with that of Mayence. The well-known intensity anomaly was clearly noted at the 4,0 band (see Fig. 14). Whether this anomaly is due to the coincidence of the γ (4,0) and the ε (0,0) band or is a true anomaly within the γ system could not be established.

Many bands belonging to the $(v',0)$ progression of the weakly absorbing β bands are either superimposed or partially overlapped by strong δ and γ bands. Therefore, very little can be deduced regarding the intensity distribution of the β bands. There seems to be a regular increase in intensity from $v' = 3$ to $v' = 10$, although $v' = 7$ and $v' = 8$ are overlapped by other bands. For $v' > 10$ there is a gradual decrease. This result, as well as that of Mayence, seems to indicate no intensity anomaly up to $v' = 11$.

The relative intensity distribution of the three known δ bands $(v' = 0,1,2)$ obtained in this experiment is in accord with that of Tanaka (1949) and Migeotte and Rosen (1950). No bands of the δ system with $v' > 2$ have been observed in absorption, and Tanaka explained this phenomenon as due to a strong interaction of the $C\,^2\Sigma$ state (see Fig. 13) with some unknown state of NO.

A number of diffuse bands were found in the region below about 1400 Å (see Fig. 16). These bands are comparatively weak and are superimposed on a moderately strong continuum. Their distribution and intensities were so irregular that it was not possible to recognize any progression; however, their diffuseness suggests predissociation or preionization. Unlike the case of the bands at longer wavelengths, the k-values for these bands were independent of pressure and, therefore, should be reliable.

5.3. ABSORPTION CONTINUA

Mayence (1952) reported a weak continuum with a maximum at 1470 Å and ascribed it to the transition $^2\Pi \rightarrow\,^2\Pi$ of NO, using 5.29 ev as the dissociation energy of NO. Figure 15 does show that there might be a continuum underlying the bands in the region from 1400 to 1600 Å. In this region, however, the vibrational bands are intense and closely spaced; hence, it is not safe to draw a conclusion from data obtained with relatively poor resolution. In fact, the k-values for the several minima in this region show an apparent pressure effect which may very well be due to lack of resolution. The k-values of several minima for several different pressures are shown in Table 3. A few values at shorter wavelengths, where there appears to be a true continuum, are also included for comparison. The k-values are fairly constant for the first three wavelengths, but this is not so for the minima at about 1389, 1419, 1469, and 1514 Å. Thus, from this data it is not possible to conclude that there is a continuum with a maximum at about 1470 Å.
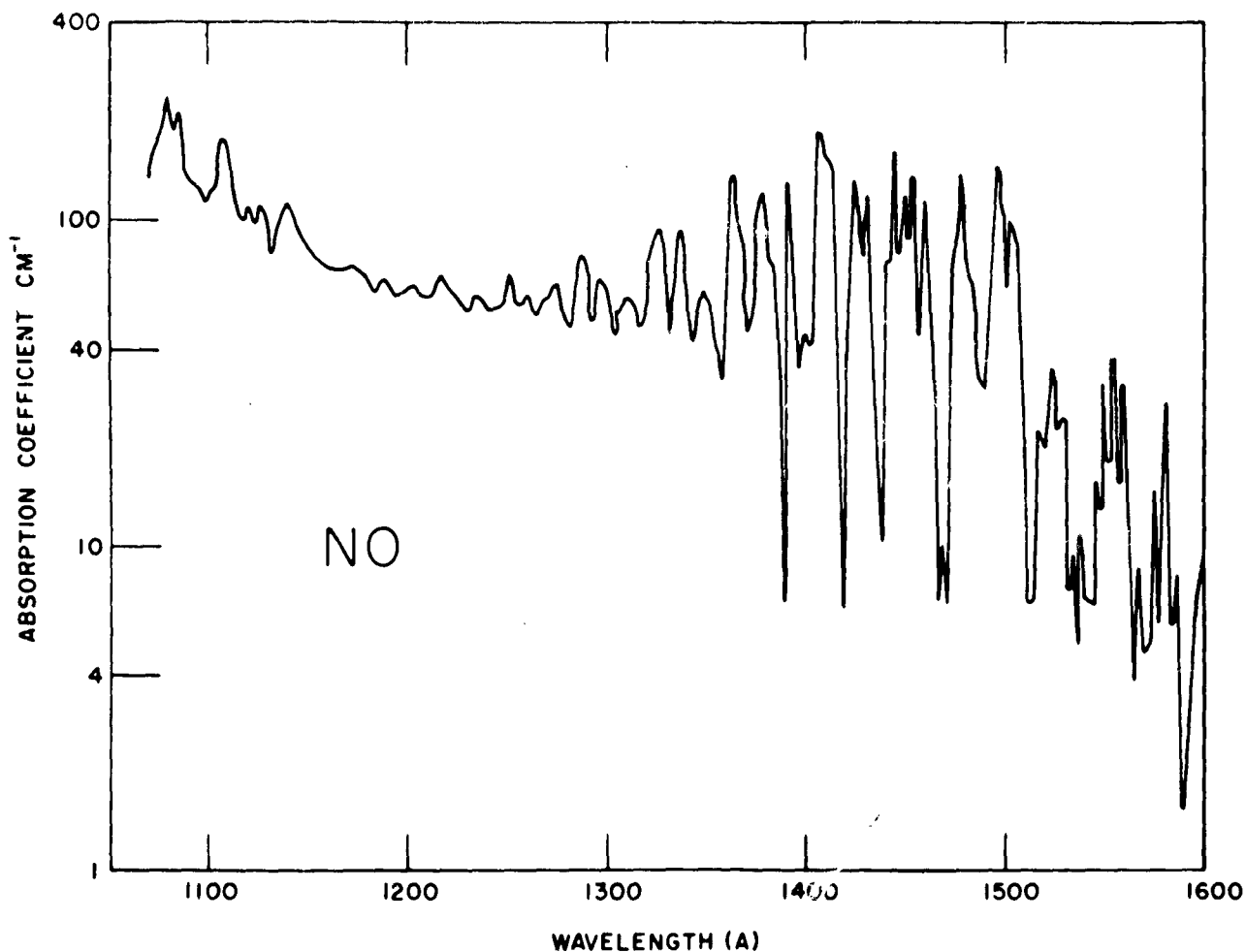
Fig. 16. Absorption coefficients of NO in the region from 1050 to 1600 Å.

Table 3. Some k-values (cm^{-1}) in the region from 1332 to 1514 Å for several pressures.

P mm Hg (Å)	0.52	0.96	1.92	4.72	7.15	10.1	23.2	33	100
1332..........	44	45	42	46	45	44			
1343.........	38	41	43	43	44	43			
1358..........	32	31	34	32	31	32			
1389..........				7.4	7.5	7.1	6.8	6.9	5.7
1419..........				12.9	10.7	9.6	8.5	8.1	5.9
1469..........			7.1	6.5	6.2	5.9	4.5	4.2	2.85
1514..........			5.4	4.9	4.4	3.9	2.85	2.39	

As shown in Fig. 16, there is a continuum in the region below about 1380 Å which has not been reported previously. Except for a few bands superimposed on the continuum near 1350 Å, the k-values were independent of pressure (factor of 20). The weak bands in the region below 1300 Å also followed Beer's law.

The continuum itself appears rather flat and may be due to overlapping of more than one continuum. The long wavelength end of the continuum is very close to the energy of dissociation products $N(^2D)$ and $O(^3P)$, so that it is plausible to attribute this continuum to the transition from the ground state to one of the allowable upper states deduced from these products by the Wigner-Witmer rule. There are several such states, including the upper state of the β bands. A rough extrapolation of the intensity curve, plotted on a linear scale from 1070 Å to the long wavelength side, terminates near 1230 Å, the energy of dissociation product $N(^2P) + O(^3P)$; so an analogous interpretation can be made for this case.

The k-value of NO at Lyman alpha is 67.5 cm^{-1}. This value might prove useful in atmospheric physics, since one of the theories on the formation of the D layer is the photoionization of nitric oxide by radiation in the region from 1100 to 1300 Å, particularly by Lyman alpha.

5.4. PHOTOIONIZATION CROSS SECTION OF NO

As pointed out previously, the first ionization potential of nitric oxide has not been measured spectroscopically. Because of the complexity of the NO spectrum, a Rydberg series could not be found. Therefore, an attempt was made to detect an ionization continuum in the region of the continuous absorption (see Fig. 16).

The preliminary experiment was simple and was carried out with the experimental arrangement already described (see Section 2.5). The cell for the ionization experiment was essentially an absorption cell provided with platinum strips for the collection of electrons and ions. Only about 5 v between the platinum plates were required to produce a saturation current; however, in most cases the voltage used was 10 v. Currents measured were in the range from 10^{-13} to 10^{-10} amp and a commercial amplifier (Beckman micro-microammeter, model RXG2) was used. The amplified current was fed into a Speedomax recorder. The slit width of the monochromator and other experimental conditions were identical with those used in the absorption measurement. Blank runs showed that the photoelectric current due to reflected or scattered light was negligibly small. For this purpose measurements were made both with the cell empty and with the cell filled with gases with high ionization potential.

To obtain the ionization yield, it is necessary to know the number of photons absorbed per second within the cell. The intensity of the light entering the cell was measured with a phosphor-coated photo-multiplier that was previously calibrated (see Section 2.2). The measured transmission of the LiF window was used in this determination. Several pressures of NO ranging from 0.49 to 10.5 mm were used, and the fraction of the incident radiation absorbed in the cell was computed from the previously determined k-values. These data were adequate to give the ionization yield which is defined here as the ratio of the number of ions formed per second and the total number of photons absorbed per second.

Table 4 shows the yield obtained at a number of wavelengths. Thus, the ionization cross section of NO in the region from 1060 to 1300 Å is of the order of 10^{-18} cm^2 which is quite large. Since there are some possibilities of systematic errors, the combined error might be large and is estimated to be about 50 percent. A more accurate determination using direct energy measurements with a thermocouple would be desirable.

The onset of ionization occurs at 1343 Å ± 2 Å or 9.23 ev ± 0.02 ev. This appears to be a more precise value of the first ionization potential of NO, than the value 9.4 ev ± 0.2 ev, obtained by Hagstrum (1951) by the electron impact method. Recently, Miescher (1952) and Tanaka (1953) independently

Table 4. Photoionization of NO.

(Å)	Yield	(Å)	Yield
1344	0.002	125?	0.45
1342	0.010	12??	0.50
1340	0.029	121?	0.51
1338	0.080	120?	0.52
13?2	0.096	115?	0.49
1315	0.14	11??	0.4?
1292	0.35	1080	0.45

reported an emission band of NO^+ ion with energy 9.05 ev. It is interesting to note that by adding this energy to the first ionization potential, one obtains the fourth ionization potential (18.28 ev) of NO found by Tanaka (1942).

6. CARBON DIOXIDE

From the scarcity of discussion in the literature, it appears that carbon dioxid.. does not play an important role in the photochemistry of our atmosphere. Perhaps it is not safe to assume this, since so little is known regarding the photochemistry of the atmosphere. Radiation in the vacuum ultraviolet region dissociates CO_2 into CO and O, and this process has been used as an actinometer for photochemical studies. In this connection, it might be noted that the atmosphere of Venus is composed almost entirely of CO_2 and receives the same ultraviolet radiation; however, the expected photochemical product, CO, has not been observed.

The absorption spectrum of CO_2 in the vacuum ultraviolet has been studied by a number of investigators including Lyman (1908), Leifson, (1926), Henning (1932), Rathenau (1934) and Price and Simpson (1938). Considerable attention has been focused on the electronic structure of the CO_2 molecule, especially by Mulliken (1932, 1935, 1942) who made theoretical formulations for this molecule.

The absorption coefficients of CO_2 in the region from 1440 to 1670 Å were measured by Wilkinson and Johnston (1950). At lower wavelengths there appears to be only the measurement of Preston (1940) at Lyman alpha.

The CO_2 used in the present investigation was prepared in a vacuum purification system by repeated sublimation of tank CO_2, retaining only the middle fraction in each sublimation. Mass spectrometric analysis showed that the total amount of impurities in the purified sample was less than one part in 2000.

The measurement of the k-values of CO_2 required no modification in the experimental method. To cover a wide range of absorption intensities, pressures of CO_2 ranging from about 0.002 to 100 mm Hg were used in the absorption cell. The pressure was varied by a factor of 10 to 50 for each wavelength, but the k-values were found to be independent of pressure over the entire spectral range investigated. Furthermore,
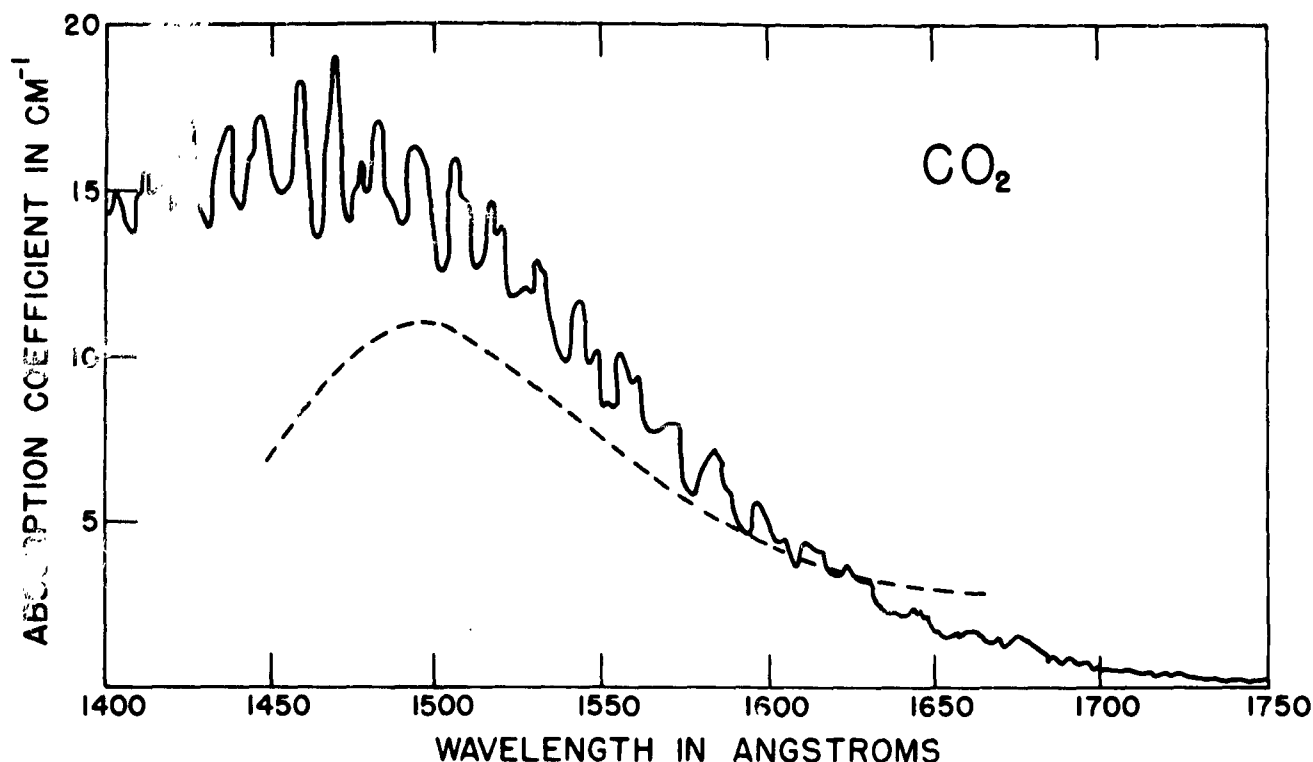
Fig. 17. The k-values of CO_2 in the region from 1400 to 1750 Å.

the data were obtained with two different gratings, one giving somewhat higher resolution than the other. The k-values in the region from 1300 to 1400 Å obtained with these gratings agreed within experimental error, thus indicating that the resolution was adequate.

For convenience of discussion, the results are divided roughly into three spectral regions: the first region covers the range from 1400 to 1800 Å which consists of a continuum and a number of weak diffuse bands; the second region, 1200 to 1400 Å, likewise has a continuum and a number of diffuse bands; and the third region at shorter wavelengths includes some very strong bands and at least one very intense absorption continuum.

6.1. RESULTS FOR THE SPECTRAL REGION FROM 1400 TO 1800 Å

The k-values of the absorption spectrum of CO_2 in this spectral region are shown in Fig. 17 by the solid curve. The results of Wilkinson and Johnston (1950) are shown by the dashed curve. Their curve should be raised about 10 percent, however, since their absorption coefficients were defined for 30° C rather than for 0° C. Even when this is done, their k-value at 1450 Å is about a factor of 2 lower, and at 1660 Å it is a factor of 2 higher than our result. They found the maximum of the continuum at 1495 Å; Price and Simpson (1938) observed the maximum at about 1460 Å. Since a number of diffuse bands are superimposed on the continuum in an apparently irregular manner, the maximum of the continuum cannot be determined precisely. By taking into account the fact that a second continuum (see Section 6.2) overlaps the first in the region from 1400 to 1450 Å, the maximum was estimated to be at about 1475 Å. The result (Fig. 17) agrees much better with the absorption spectrum of Price and Simpson than with the curve obtained by Wilkinson and Johnston.

Using Eq. (1), the f-value of 0.0043 was obtained for the continuum (excluding the bands and subtracting the contribution of the second continuum). This value is in good agreement with the value of 0.004 obtained by Wilkinson and Johnston (1950) in spite of the differences in the absorption curves. Fuchs (1927) has obtained a resonance wavelength of 1480 Å for CO_2 from dispersion measurements. However, the corresponding f-value (0.075) is much higher than the values obtained by absorption measurements, and Wilkinson and Johnston have pointed out the need for a revision in the dispersion equation. The small f-value indicates a forbidden transition which Mulliken (1935, 1942) has already suggested: $^1\Sigma_g^+ \rightarrow (\Pi_g)^{-1}\sigma_g$, $^1\Pi_g$. He has also suggested the possibility that such a forbidden transition may occur weakly if the upper state of the equilibrium form of the CO_2 molecule is triangular.

The bands overlying the continuum have not been classified, and in fact some investigators have not observed most of them. Leifson (1926) observed bands at 1692, 1675, 1660 and 1647 Å, and Wilkinson and Johnston (1950) observed bands at 1690, 1673 and 1662 Å. On the other hand, Price and Simpson (1938) did not list the wavelengths of the bands in this region, although their photograph seems to show most of the bands observed in the present investigation. These bands appear irregular and diffuse, hence it is difficult to single out any vibrational progression. Most of them are listed in Table 5 along with the other observed bands. In this table, the first column represents the approximate wavelength of the "middle" of the band, the second column is the relative intensity of the band taking the strongest band at 1088 Å as 1000.

Table 5. Wavelengths (in Å) of CO_2 absorption bands. Wavelengths given by Rathenau (1934), Price and Simpson (1938), Leifson (1926) and Wilkinson and Johnston (1950) are indicated by their initials.

λ	I	λ by others	λ	I	λ by others	λ	I	λ by others	λ	I	λ by others
1072	70	1074(R)	1227	<1		1403	1		1549	<1	
1081	50	1083(R)	1244	<1		1413	1		1555	1	
1088	1000	1089(R)	1252	<1		1418	<1		1570	<1	
1093	20	1093(R)	1262	<1		1422	<1		1584	1	
1101	20	1103(R)	1272	2		1426	1		1596	<1	
1110	90	1112(R)	1284	2		1436	1		1605	<1	
1119	800	1121(R),1120(P&S)	1293	5		1447	1		1613	<1	
1129	400	1129(R),1130(P&S)	1303	5		1459	<1		1628	<1	
1142	100	1142(R)	1316	3		1469	1		1645	<1	1647(L)
1150	20	1149(R)	1328	3		1478	<1		1651	<1	1660(L),1662(W&J)
1158	30	1157(R)	1336	4		1483	1		1669	<1	
1166	40	1165(R)	1341	2		1495	1		1675	<1	1675(L),1673(W&J)
1175	10	1174(R)	1349	3		1506	1		1686	<1	
1183	60		1362	2		1517	1		1691	<1	1692(L),1690(W&J)
1193	<1		1371	1		1520	1		1695	<1	
1203	<1		1381	1		1526	<1		1708	<1	
1210	<1		1386	<1		1531	1		1715	<1	
1217	<1		1394	<1		1543	1		1720	<1	
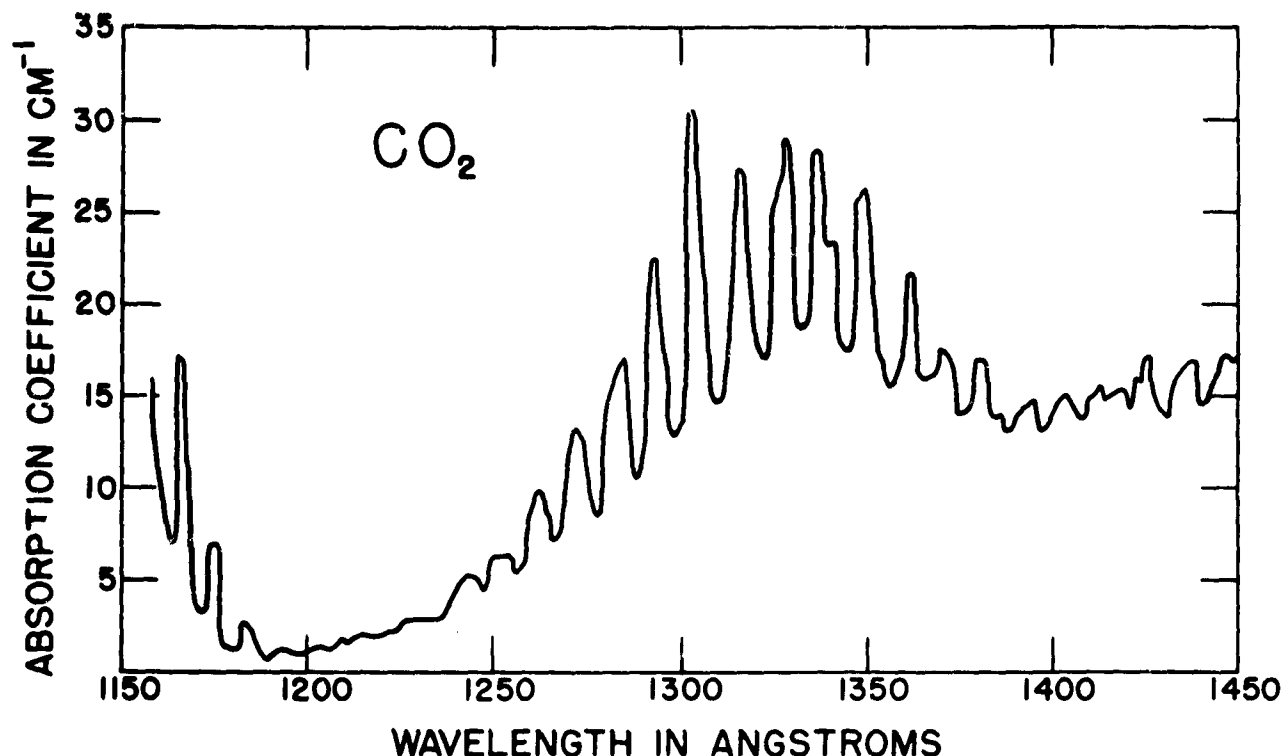
Fig. 18. The k-values of CO_2 in the region from 1150 to 1450 Å.

and the last column gives the wavelength given by other observers. The table must be considered tentative, since further investigations are required.

6.2. RESULTS FOR THE SPECTRAL REGION FROM 1200 TO 1400 Å

The second continuum (λ_{max} at 1332 Å) shown in Fig. 18 is a little more intense than the 1475 Å continuum. The relative intensities of these two continua do not seem to agree with the result of Price and Simpson (1938). In their photograph of the absorption spectrum of CO_2 at very low pressures (~0.01 mm), the 1332 Å continuum is not present while the 1475 Å continuum appears. This may be explained by the possible changes in the background intensity of the Lyman continuum.

The f-value for the 1332 Å continuum computed as in the previous case was 0.0053, which is slightly larger than that of the first continuum. This low value may again be indicative of a forbidden transition to a second excited electronic state.

The bands in this region are somewhat more intense and appear more regular than those in the first region. Price and Simpson (1938) suggested that these bands may consist of two progressions starting from 1380 Å and 1368 Å, respectively, each with a frequency interval of about 1225 cm^{-1} corresponding to the symmetrical vibration frequency of the ground state. An attempt to follow their suggestion was not successful, however, since the shape of the bands and wavelength intervals is too irregular for wavelength assignments.
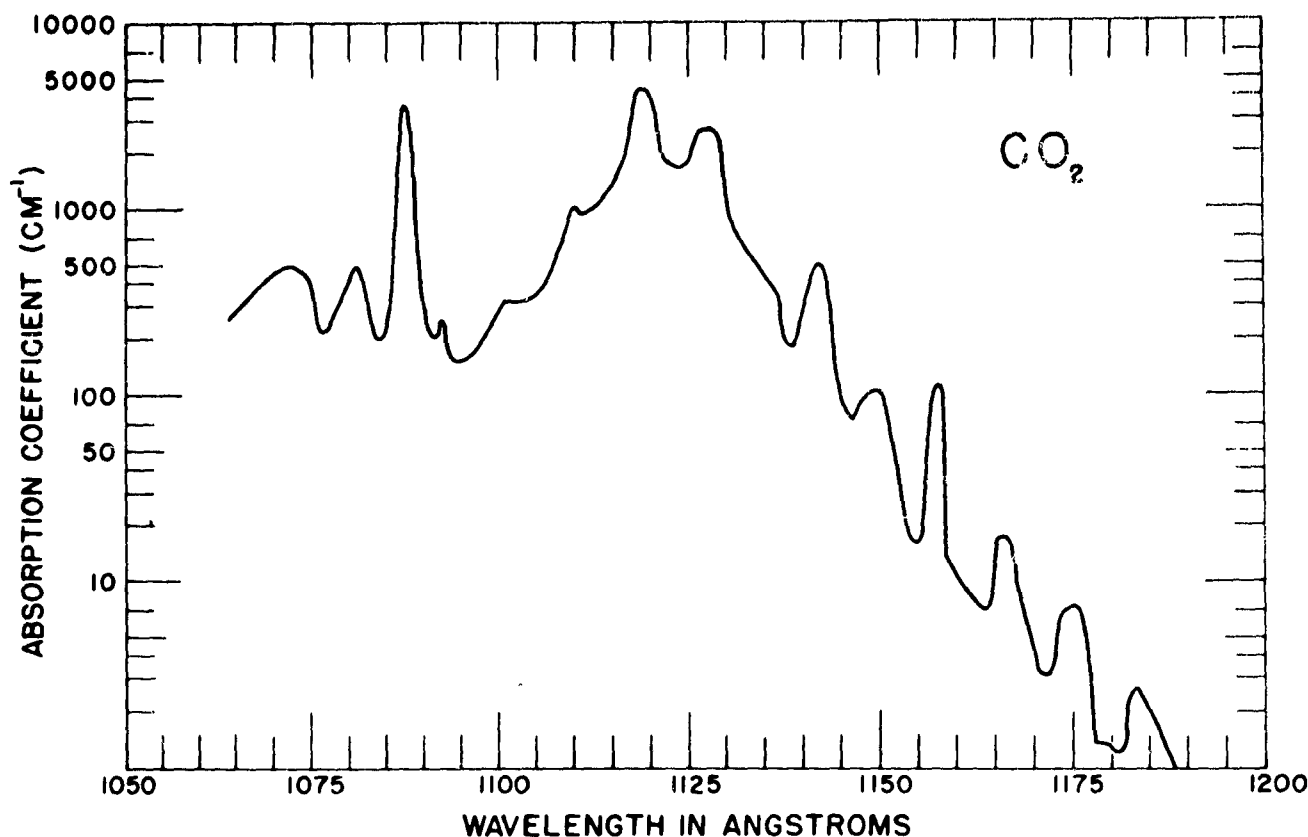
Fig. 19. The k-values of CO_2 in the region from 1050 to 1200 Å.

The k-value at Lyman alpha which lies near the minimum on the short wavelength side of the continuum was found to be 1.97 cm^{-1}. This value agrees within experimental error with the carefully measured value (2.01 cm^{-1}) of Preston (1940).

6.3. RESULTS FOR THE SPECTRAL REGION FROM 1050 TO 1200 Å

Extremely high absorption coefficients were obtained in this region as shown in Fig. 19 which is a semi-log plot of the k-values. The highest k-value was about 4350 cm^{-1} at 1119 Å.

The continuum with its maximum at about 1121 Å is much more intense than the two continua at longer wavelengths. The f-value computed for this continuum was 0.12 and this value indicates that the continuum is an allowed electronic transition.

The strong bands overlying the 1121 Å continuum have been previously reported by Rathenau (1934) and Price and Simpson (1938). The strong bands at 1119 and 1129 Å have been shown by the latter to contain the second members of a Rydberg series converging to the first ionization potential at 13.73 ev. The other bands have not been classified. Our data, however, seem to show a progression with a frequency interval of about 630 cm^{-1} which would correspond to the bending vibration in the ground state.

Below 1100 Å there appears to be a portion of another strong continuum. However, the data obtained in this region are somewhat poor because of absorption of the LiF windows of the absorption cell, and data obtained in the region from 1050 to 1080 Å were rejected.
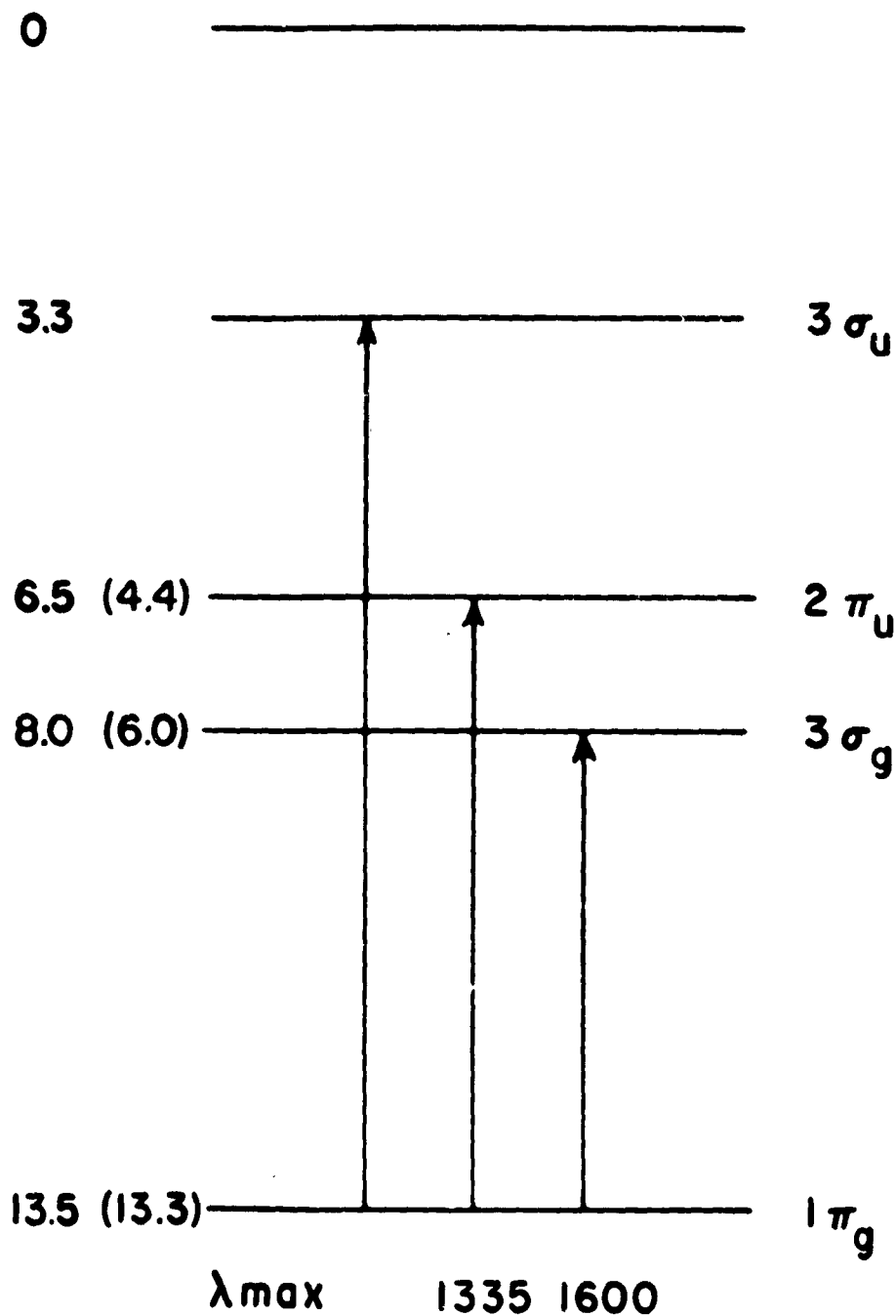
Fig. 20. Predicted electronic
transitions for CO₂.

6.4. DISCUSSION ON ELECTRONIC TRANSITIONS

It is possible to make some comparisons of our results with certain theoretically predicted electronic transitions suggested by Mulliken (1942). A portion of one of the energy diagrams used in his paper is reproduced in Fig. 20, showing only the outermost occupied level of CO₂ and three unoccupied ones. The column on the right designates the molecular orbital and the column on the left the ionization energy in electron volts (averaged for CO₂ and CS₂) corresponding to each orbital. The values in parentheses are the ionization energies for the CO₂ molecules which Mulliken gives for the *vertical* processes corresponding to

Table 6. Dissociation energies of CO_2 in electron volts.

States	Calculated Values	Experimental Values (Upper Limit)
$CO(^1\Sigma) + O(^3P)$	5.4	6.8
$CO(^1\Sigma) + O(^1D)$	7.4	7.7
$CO(^1\Sigma) + O(^1S)$	9.7	10.3

the absorption maxima at 1600 and 1335 Å (from the data of Price and Simpson). Instead of 1600 Å if the value 1475 Å or 8.4 ev, corresponding to the maximum of the first continuum, is used for the $1\pi_g \rightarrow 3\sigma_g$ transition, we obtain the ionization energy

$$13.7 - 8.4 = 5.3 \text{ ev}$$

for the $3\sigma_g$ orbital. For the $1\pi_g \rightarrow 2\pi_u$ transition our results are substantially the same as Mulliken's, since the wavelengths used for the second maximum are about the same (1332 and 1335 Å). The absorption maximum at 1121 Å (11.1 ev) seems to correspond to the transition $1\pi_g \rightarrow 3\sigma_u$ energetically. This would give for the ionization energy of the $3\sigma_u$ orbital a value of about $13.7 - 11.1 = 2.6$ ev.

The dissociation energy can be measured from the long wavelength limit of a continuum. In practice, this is often neither possible nor reliable. Even when the case is not an ideal one, a good estimate of the upper limit of the dissociation energy can be obtained, provided that the extrapolation is not too extensive. Using this method, dissociation energies (upper limits) of 6.8, 7.7 and 10.3 ev were obtained from the three continua. These may be compared with the values listed by Weeks (1949) as shown in Table 6.

The values for the lowest dissociation energy do not agree too well. This may be explained by the possibility that the absorption continuum arises from a transition to a relatively steep repulsive curve for the dissociation products $CO(^1\Sigma) + O(^3P)$. In fact, Weeks shows such a curve for this dissociation. The two higher dissociation energies are in good agreement, considering the fact that the experimental values are upper limits.

7. NITROUS OXIDE

The presence of nitrous oxide in our atmosphere is now well established. The first observation was made by Adel (1939) who attributed an atmospheric band at 7.8 μ to N_2O, and since then his observation was confirmed by a number of investigators who also observed other infrared bands of N_2O in the solar spectrum. The total amount of N_2O in the atmosphere corresponds to about a layer thickness of 4 mm reduced to NTP according to McMath et al. (1950). The origin, amount and distribution are not sufficiently well known to establish the importance of N_2O in the photochemistry of our atmosphere. The possibility of the formation of NO from N_2O was pointed out at the beginning of Section 6.

A few investigators have studied the absorption spectrum of N_2O in the vacuum ultraviolet. Leifson (1926) observed two continuous bands, the first covering the region from 2000 to 1680 Å and the second extending from 1550 Å to the transmission limit of fluorite. However, he did not observe any discrete
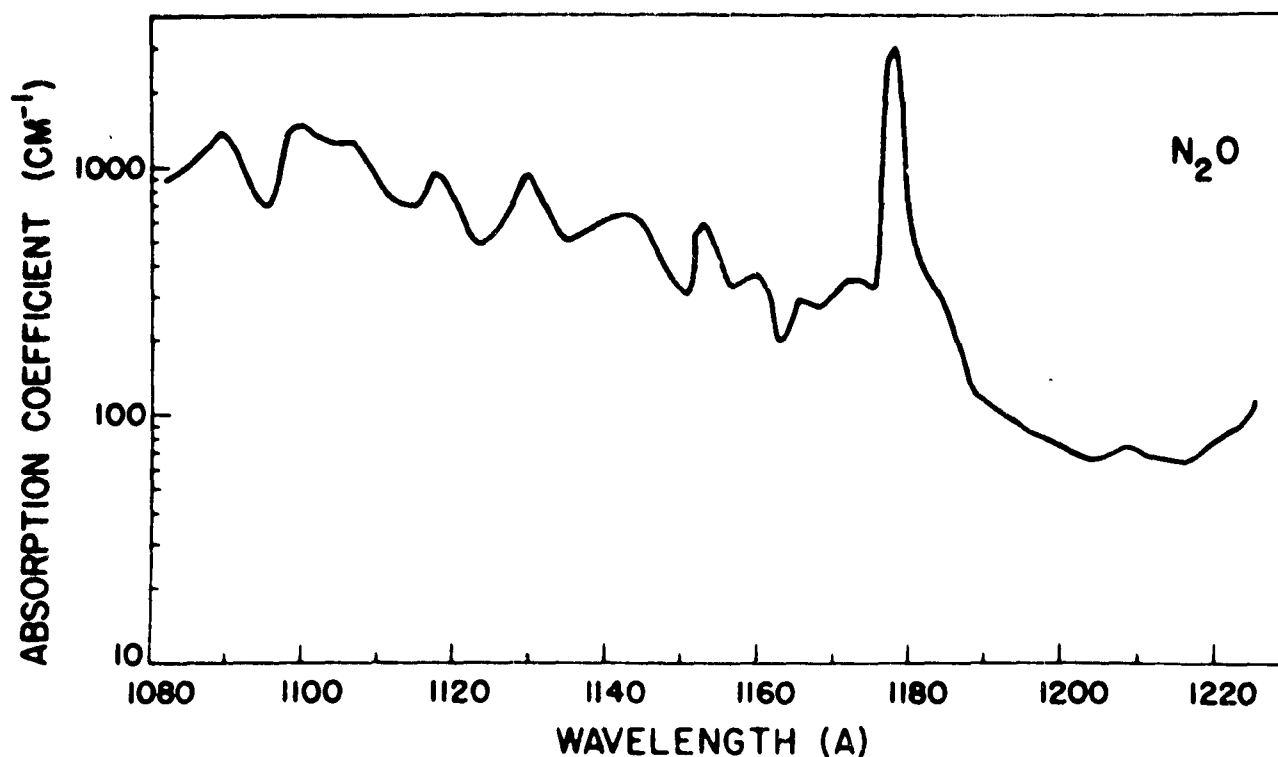
Fig. 21. The k-values of N₂O in the region from 1080 to 1220 Å.

bands. Sen-Gupta (1935) also observed two continua in about the same regions. The most thorough and detailed work is that of Duncan (1936) who studied the region from 850 to 2200 Å   On the other hand, the near-ultraviolet absorption spectrum of N_2O has been studied by a number of investigators.

The absorption coefficients of N_2O in the region from 1390 to 2200 Å were recently measured by Romand and Mayence (1949). They measured the k-values of the two continua mentioned above and found maxima at 1450 and 1840 Å. There appear to be no other measurements of k-values in the vacuum ultraviolet.

In the present investigation, the N_2O was purified from tank gas by drying over P_2O_5 and ten successive fractional distillations with liquid nitrogen, retaining the middle fraction each time. The final product was analyzed with a mass spectrometer. No detectable impurities were found, indicating that the total impurities could not exceed 0.05 percent.

Absorption coefficients were measured from 1080 to 2100 Å using pressures from about 0.01 to 200 mm Hg, to cover the absorption intensities. Beer's law was found to hold over the entire spectral range, within experimental error of 5 to 10 percent.

For convenience of discussion, the absorption spectrum of N_2O will be divided into four regions, each of which will be designated by the terminology of Duncan (1936). Pegion E-F will cover the range from 1080 to 1215 Å, region D from 1215 to 1380 Å, region C from 1380 to 1600 Å and region B from 1600 to 2100 Å.

7.1. RESULTS FOR REGION E-F

Figure 21 is a semilog plot of k vs λ from 1080 to 1215 Å. Wavelengths below this region could not be studied in this work, since the transparency of LiF extends only to about 1050 Å. Rather diffuse bands
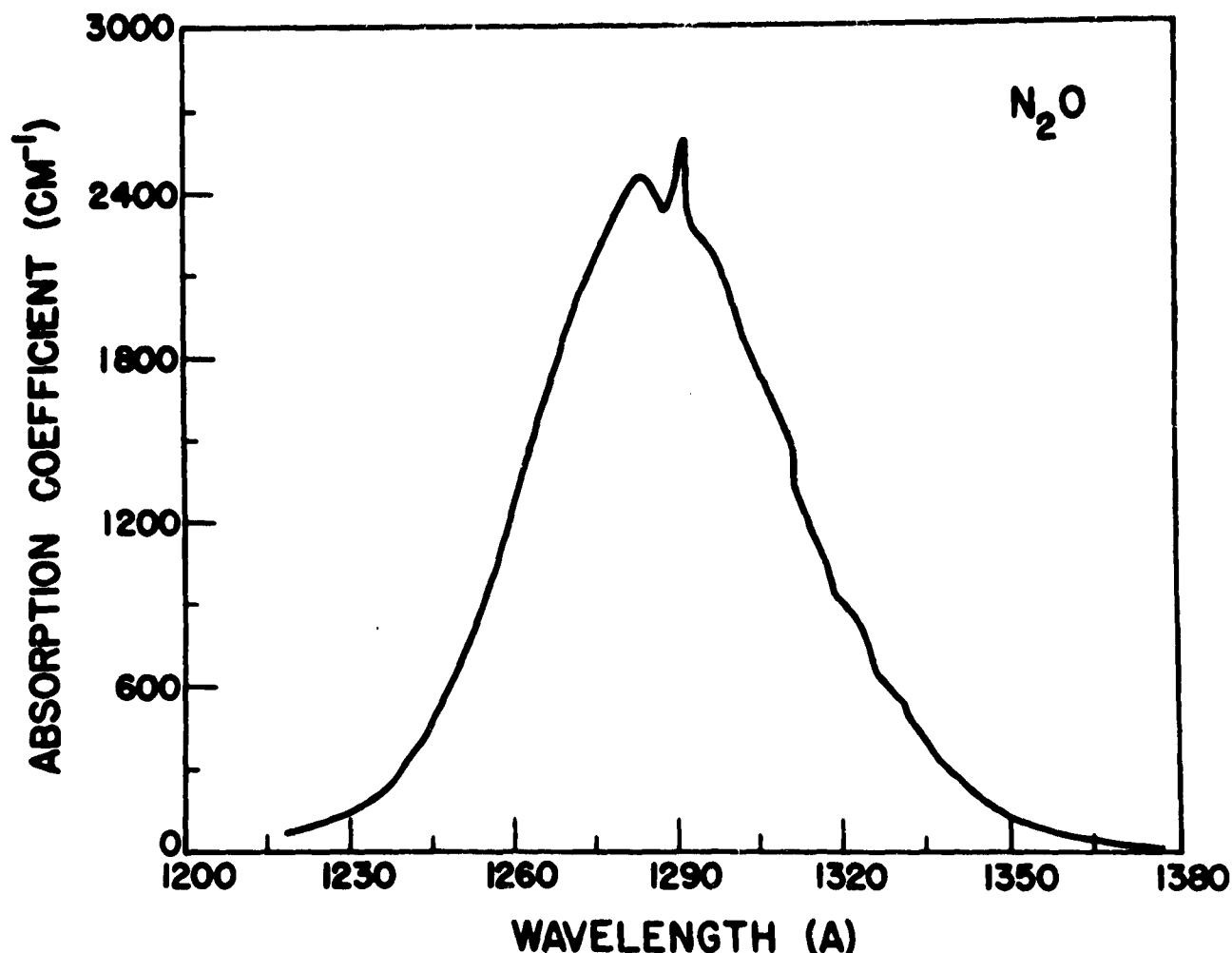
Fig. 22. The k-values of N_2O in the region from 1220 to 1380 Å.

were found at wave numbers 85,350; 85,800; 86,200; 86,700; 87,500; 88,500; 89,450; 90,400; 91,000 and 91,800 cm^{-1}. Nearly all of these bands appear in the photograph of Duncan's paper. The wave numbers of the bands agree quite well with those Duncan has given except for the bands at 88,500 and at 91,000 cm^{-1}. For the latter, he gives the value 91,200 cm^{-1}. According to Duncan, this band is a member ($n = 4$) of a Rydberg series represented by

$$\nu = 102,567 - \frac{R}{(n - 0.92)^2} \text{ where } n = 3, 4, 5 \ldots \tag{2}$$

The calculated wave number for $n = 4$ is 90,999 cm^{-1}, in closer agreement with our value of 91,000 cm^{-1}. It must be admitted, however, that the wave numbers of the bands in this spectral region are only approximate values, owing to the diffuse nature of the bands. Therefore, it was not possible to classify them. They may be due to one or more electronic transitions.

In this region there is another band at 84,900 cm^{-1} which is the strongest ultraviolet absorption band observed for N_2O. Its k-value at the maximum is 3010 cm^{-1}. Duncan (1936) suggested that it is a member of a Rydberg series converging to an ionization potential at a wavelength below our limit of observation.
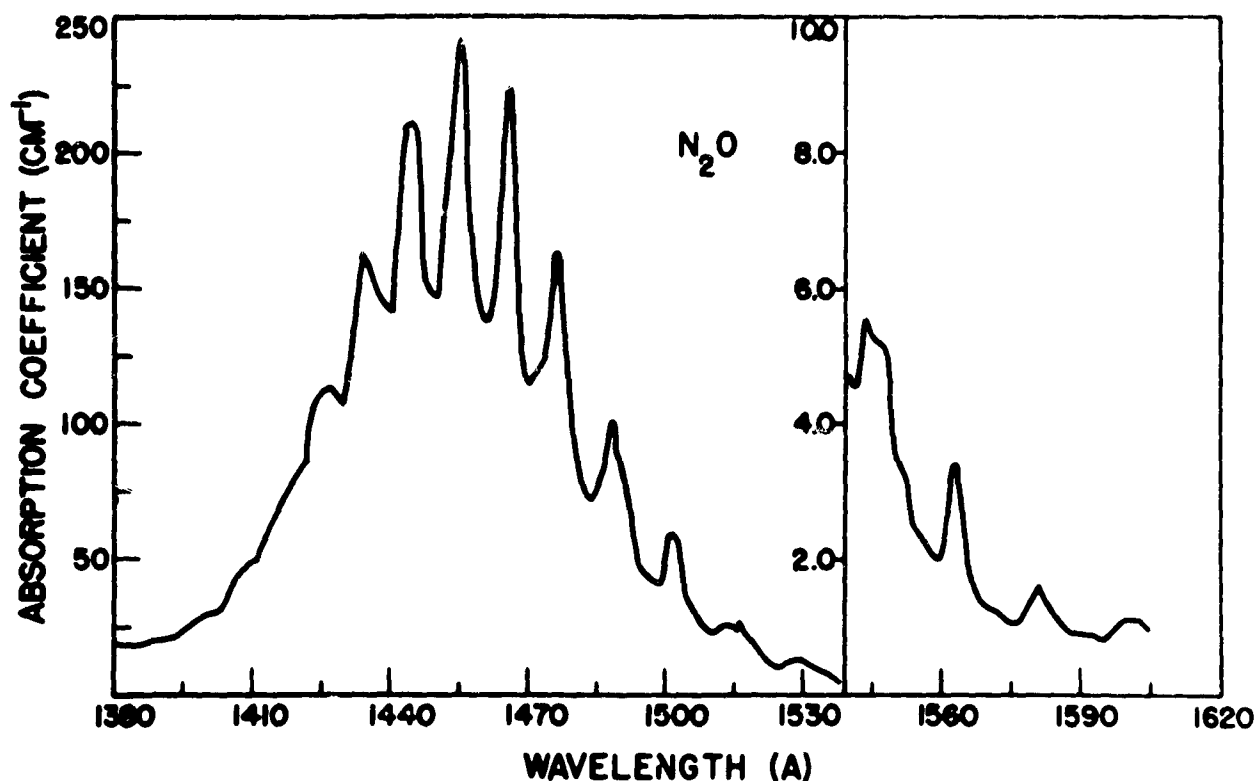
Fig. 23. The *k*-values of N₂O in the region from 1380 to 1600 Å.

Most of the absorption intensity in this spectral region may be attributed to a continuum which appears to underlie the diffuse bands. The maximum of the continuum cannot be established from Fig. 21. However, Duncan's photograph shows a relatively transparent region at about 1060 Å. and it appears that the absorption intensity of the continuum decreases rapidly from 1080 to 1060 Å. Thus, the shape of the absorption curve for the continuum is inferred to be quite asymmetric. The maximum of the curve is probably near 1080 Å. On this basis, the f-value of the continuum (excluding the bands) was estimated to be about 0.1 (see Eq. (1)) which indicates an allowed transition.

7.2. RESULTS FOR REGION D

Figure 22 is a linear plot of k vs λ from 1215 to 1380 Å. Whereas Duncan has reported this region to contain a perfectly smooth continuum having no structure, the present study has located several weak diffuse bands on its long wavelength slope and one sharp band at 77,400 cm⁻¹ which may be a member of the Rydberg series described by Eq. (2). Duncan chose the maximum absorption of the continuum at 77,900 cm⁻¹ as his Rydberg member ($n = 3$). The band at 77,400 cm⁻¹ fits the Rydberg series much more closely than does the continuum maximum at 77,900 cm⁻¹, the calculated value being 77,202 cm⁻¹. It is possible that this band is very strong and that the continuum is actually somewhat weaker, with its maximum value appearing to be high because of poor resolution of the sharp band. The absorption of the Rydberg band probably contributes to the maximum value of the continuum ($k = 2465$ cm⁻¹). Diffuse bands are found at 77,100; 76,250; 75,600 and 75,100 cm⁻¹. The wave numbers given here are probably not very accurate,

Table 7. Bands of electronic transition C of N₂O.

n	Calculated	Observed	Δν	Relative Intensity
0	59,590	59,520	70	0.06
1	60,565	60,510	55	0.08
2	61,484	61,580	−96	0.18
3	62,349	62,460	−111	0.20
4	63,164	63,250	−86	0.68
5	63,931	64,020	−89	1.68
6	64,654	64,720	−66	1.60
7	65,337	65,360	−23	5.0
8	65,981	65,980	1	8.0
9	66,591	66,580	11	24
10	67,173	67,160	13	43
11	67,720	67,700	20	70
12	68,246	68,210	36	102
13	68,749	68,730	19	102
14	69,234	69,230	4	69
15	69,703	69,710	−7	44
16	70,160	70,180	−20	17
17	70,609	70,650	−41	1
18	71,050	71,100	−50	1
19	71,490	71,530	−40	1
20	71,930	71,940	−10	1

owing to the diffuse nature of these bands. It is possible that region D consists of more than one electronic transition with the upper state of one being repulsive. In addition, the sharp, strong band is tentatively taken as a Rydberg series member. Neglecting the Rydberg band an ' the possibility that the continuum may be somewhat weaker than it appears to be, the f-value of the continuum is calculated to be 0.367. The limits of integration are $\nu = 82,250$ cm⁻¹ and $\nu = 73,000$ cm⁻¹. The high f-value suggests an allowed transition.

7.3. RESULTS FOR REGION C

Figure 23 is a linear plot of k vs λ for this region. This region is composed of a continuum on which about 20 diffuse bands are superimposed. Duncan (1936) reported nine bands which fit the formula

$$\nu = 65,939 + 621.2\,n - 11.54\,n^2 \quad (n = 0,1,2\ldots).$$ (3)

He was not able to relate the frequency 621 cm⁻¹ to the fundamentals (589, 1285 cm⁻¹) observed in the infrared, and suggested that the value he obtained was probably a modification of 589. Sponer and Teller (1941) suggested two other possibilities: (1) that the observed bands may represent two systems, each with 621×2 cm⁻¹ spacing; and (2) that the bands observed by Duncan were possibly not the lowest members of
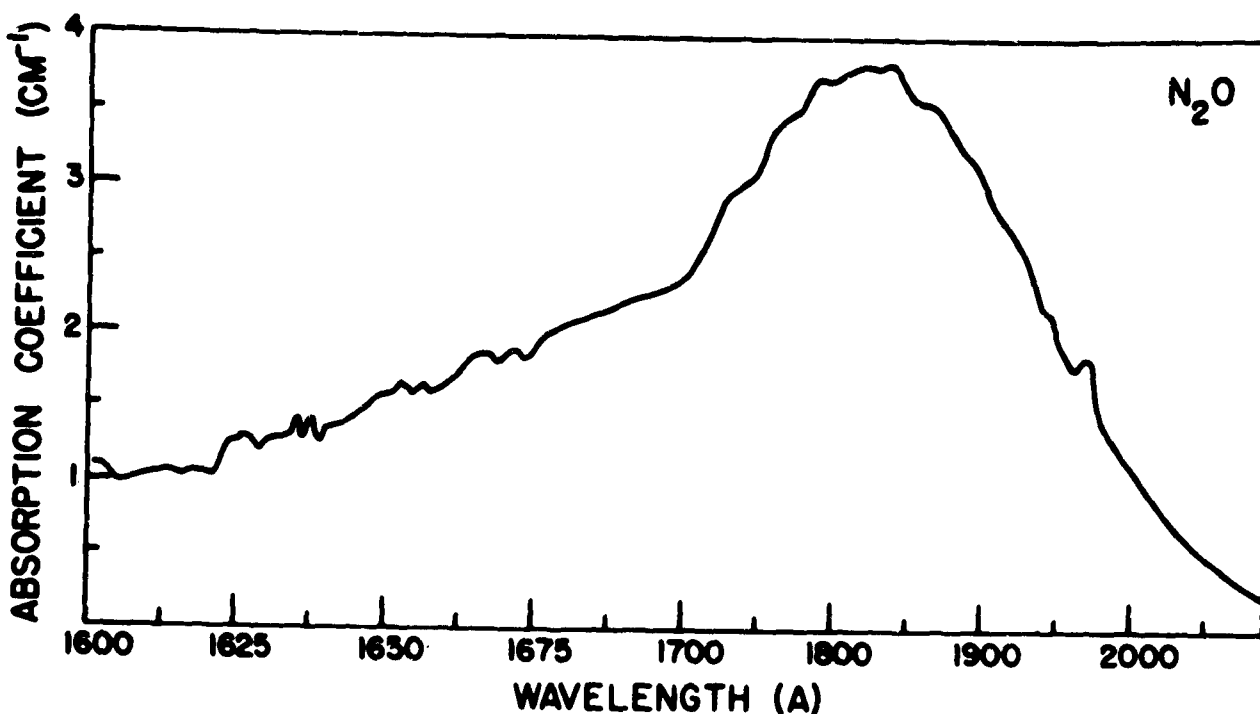
Fig. 24. The k-values of N₂O in the region from 1600 to 2100 Å.

the progression, in which case there might be considerable anharmonicity leading to a lowering of 1285 cm⁻¹.

The present work has detected many more bands in this region, both at the shorter and longer wavelength sides of the region where Duncan found 9 bands. These bands are listed in Table 7 and they approximately fit the equation,

$$\nu = 59,590 + 1005\, n - 30.0\, n^2 + 0.53\, n^3, \text{ where } n = 0, 1, 2 \ldots \ldots \tag{4}$$

Some of the bands which fit Eq. (4) are in region B.

The value 1005 cm⁻¹ seems to be consistent with suggestions (2) above by Sponer and Teller. The discrepancies between calculated and observed frequencies are not surprising, in view of the diffuse nature of these bands. The strongest absorption lies at the band 68,730 cm⁻¹.

There appears to be a relatively strong continuum underlying these bands with a maximum absorption coefficient of 147 cm⁻¹ at 68,940. This value compares fairly well with that of Romand and Mayence (1949) who found the k-value 118 cm⁻¹. The discrepancy might be attributed to the difference between photographic and photoelectric detection. The continuum is quite symmetrical and both ends can be extrapolated to zero without much difficulty. The f-value was measured as 0.0211, suggesting a fairly allowable transition. The limits of integration were $\nu = 73,000$ cm⁻¹ and $\nu = 64,250$ cm⁻¹.

7.4. RESULTS FOR REGION B

Figure 24 is a linear plot of k vs λ for this region. This region is one of weak continuous absorption with a maximum k-value of 3.82 cm⁻¹ at 1820 Å. Romand and Mayence found a maximum at 1840 Å with $k = 3.13$ cm⁻¹. Here, as in the preceding section, the discrepancy is probably due to the difference in method of detection. Once again, superimposed on this continuum are weak, very diffuse bands. Because of their diffuse nature, the wavelengths could not be measured accurately, and no attempt was made to classify

them. The f-value (0.0015) of the continuum was measured as in the previous section with integration limits $\nu = 65,000$ cm^{-1} and $\nu = 46,000$ cm^{-1}. The limits are probably not accurate, particularly the long-wave limit. Various authors have found different results for this value. The weak character of the absorption suggests that the transition is forbidden. It is difficult to say whether there are one or two electronic transitions involved here, although there seem to be two, with the upper state of one being repulsive and the upper state of the other having a minimum.

8. NITROGEN AND HYDROGEN

Very few absorption measurements of nitrogen and hydrogen in the Schumann region have been reported in the literature. This is due to the fact that both gases are relatively transparent in the spectral region above about 1000 Å. On the other hand, many investigators have studied these molecules, using their emission spectra both in the vacuum ultraviolet and in the longer wavelength region. Most of their results on the energy states of these molecules are summarized in the book by Herzberg (1950).

In the present work, it was not possible to obtain quantitative k-values for both gases, since the equipment used was not designed to resolve the fine structures of the observed bands. The small amount of data, however, may provide some idea of the order of magnitude of the absorption intensities of the two gases.

8.1. NITROGEN

The so-called Lyman-Birge-Hopfield bands (a forbidden transition, $X\ ^1\Sigma_g^+ \rightarrow a\ ^1\Pi_g$) were observed by Birge and Hopfield (1928) in absorption. They used an absorption path length of 100 cm and a nitrogen pressure of 300 mm Hg. The ten bands, 0,0 to 9,0, which appear in their photograph are narrow, sharp bands. About the same time, Sponer (1927) also observed these bands using a path length of 100 cm and a pressure of 100 mm Hg. It is to be noted that Sponer did not find appreciable absorption by nitrogen with a 10-cm absorption cell filled with N_2 at a pressure of 800 mm. Thus, it appears that a much larger product of path length and pressure is required to find new absorption bands in this region.

Recently, Clark (1952) reported k-values of N_2 at 27 wavelengths in the region from 584 to 1026 Å, and Weissler, Lee and Mohr (1952) reported k-values at 88 wavelengths in the region from 303 to 1306 Å. Since different light sources were used, comparison can be made only at two wavelengths (1025.7 Å and 584.3 Å). The former obtained 8 and 480 cm^{-1} while the latter obtained 60 and 700 cm^{-1}, respectively, at the two wavelengths.

The data by Weissler, Lee and Mohr give k-values at 11 wavelengths in the region above 1100 Å, the values ranging from about 5 to 160 cm^{-1}. Most of the values are for wavelengths lying between the heads of the Lyman-Birge-Hopfield bands. For example, they obtained a k-value of 66 cm^{-1} at 1215.129 Å, which lies between the 8,0 band (1226.6 Å) and the 9,0 band (1205.3 Å). This would indicate that there are absorption lines in the regions which have been considered quite transparent. Preston (1940) found

Table 8. The apparent k-values of the Lyman-Birge-Hopfield bands.

Band	k	Band	k	Band	k
0,0	0.08	4,0	0.09	8,0	0.02
1,0	0.09	5,0	0.08	9,0	0.02
2,0	0.11	6,0	0.09	10,0	0.02
3,0	0.07	7,0	0.03	11,0	0.02

that the k-value of N_2 at Lyman alpha (1215.6 Å) is less than 0.005 cm^{-1}. Since nitrogen is a major constituent of our atmosphere, much more data on its absorption intensity seem to be required.

In the present experiment, the cell length was 4.7 cm and the highest pressure of N_2 was about 500 mm Hg, the product being about one-tenth that used by Birge and Hopfield (1928). At this pressure, a weak but measurable absorption of the Lyman-Birge-Hopfield bands from 0,0 to 11,0 was observed. The bands appeared narrow (5 Å or less) and no other absorption was detected between the bands. This was consistent with the absorption spectrum obtained by Birge and Hopfield (1928) and, furthermore, the data gave no indication of impurities. At Lyman alpha the k-value was found to be definitely less than 0.01 cm^{-1} in agreement with Preston (1940).

The apparent k-values of the peaks of the Lyman-Birge-Hopfield bands are listed in Table 8. As was pointed out, these k-values are certainly not quantitative. Considering the type of data, the intensity distribution is roughly in agreement with the photograph of Birge and Hopfield. Table 8 shows an abrupt change in the band intensities going from the 6,0 band to the 7,0 band, the energy of the wavelength region between these two bands being about 9.8 ev. It is interesting to note that predissociation at about this level has been observed by Herman (1943, 1945) and by Herzberg and Herzberg (1947) in emission spectra.

One result which can be stated with some confidence is that no continuous absorption in the region from 1600 to 1050 Å with k-value greater than 0.01 cm^{-1} was observed for N_2.

8.2. HYDROGEN

Still less can be said about the absorption of H_2 in the same spectral region. Dieke and Hopfield (1927) and Tanaka (1944) studied the absorption spectrum of H_2 which extends into this region. The first four members of the Lyman bands appear in the region from 1050 to 1110 Å. These bands were observed at a pressure of about 50 mm Hg in our absorption cell. Hence, their absorption intensities appear to be about ten times greater than those of the first seven members of the Lyman-Birge-Hopfield bands of N_2.

Incidentally, the absorption data for H_2 showed some absorption bands of H_2O. Using the k-values of H_2O the amount of this impurity was found to be about one part in 10^4 which was just beyond the sensitivity limit of the mass spectrometer. This shows that in certain cases it is possible to detect quantitatively small amounts of impurity by absorption measurements in the vacuum ultraviolet. For example, one part of H_2O in 10^6 parts of rare gas or other transparent gas can be detected with a slight modification in the system used.

9. CARBON MONOXIDE *

In emission spectra, the carbon monoxide molecule is one of the most thoroughly studied diatomic molecules. Very few investigations have been made in absorption, however, because of the fact that its absorption spectrum lies mainly in the vacuum ultraviolet. Further investigation of the absorption spectrum of CO is desirable to determine its highly excited states, ionization potentials and dissociation energies that are uncertain or unknown. For example, a number of values have been proposed for the dissociation energy of CO, mostly from the study of predissociation in emission spectra, but the correct value is not known with certainty. This value would be very useful in the study of other molecules with the carbon-oxygen bond.

Unlike N_2 and H_2, CO has a rich absorption spectrum in the spectral region from 1100 to 1600 Å. There are many strong bands, particularly the well-known IVth positive bands. Because of their sharpness, however, very little quantitative data were obtained in the present absorption measurements.

The CO sample for the absorption measurement was prepared by dropping formic acid into concentrated sulfuric acid. The sample was analyzed with a mass spectrometer and found to contain less than 0.1-percent impurity. Pressures of CO from 2 to 300 mm Hg were used in the absorption cell.

For convenience of discussion, the result will be considered in terms of two spectral regions. The data are summarized in Fig. 25 which covers the region from 1060 to 1600 Å. The ordinate is labeled "absorption intensity," since the k-values were apparent ones and were obtained with insufficient resolution.

9.1. RESULTS FOR THE SPECTRAL REGION FROM 1170 TO 1600 Å

There were a number of sharp bands predominating this region. Most of them belonged to the fourth positive bands ($X\ ^1\Sigma \rightarrow A\ ^1\Pi$). The members of the v'-progression (with $v'' = 0$) from $v' = 0$ to $v' = 17$ were observed. As shown in Fig. 25, the first five bands of this progression are about equally intense in absorption, and they are the strongest bands in the entire spectral region. The 5,0 band is much weaker than the 4,0 band. Between the 13,0 and 14,0 bands, there is another abrupt change in intensity. It is interesting to note that these intensity anomalies correspond to two of the bands in which predissociations were observed. Namely, Schmid and Gerö (1938) have observed predissociation phenomena at $v' = 4, 9$ and 13 in the upper state of the fourth positive bands. Using emission spectra, Schmid and Gerö stated that the last vibrational level of the $A\ ^1\Pi$ state must be $v' = 13$, since they did not observe emission bands originating from $v' > 13$. In the present work, the bands were observed up to $v' = 17$; however, bands with $v' > 13$ were very weak.

There appears to be a weak continuum in the region from 1300 to 1600 Å underlying the fourth positive bands. This continuum resembles the Schumann-Runge continuum. If this is the case, the amount of O_2 computed from its k-value is about one part in a thousand. Although the spectrum shown in Fig. 25 is quite complex in the region below 1300 Å, there are a few bands that might be due to oxygen. Their intensities indicate, however, that the amount of O_2 is somewhat less than the above estimate. Therefore, the presence of O_2 in the sample seems probable, and the amount is somewhat less than indicated by the

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* Dr. Y. Tanaka analysed the data for this gas.
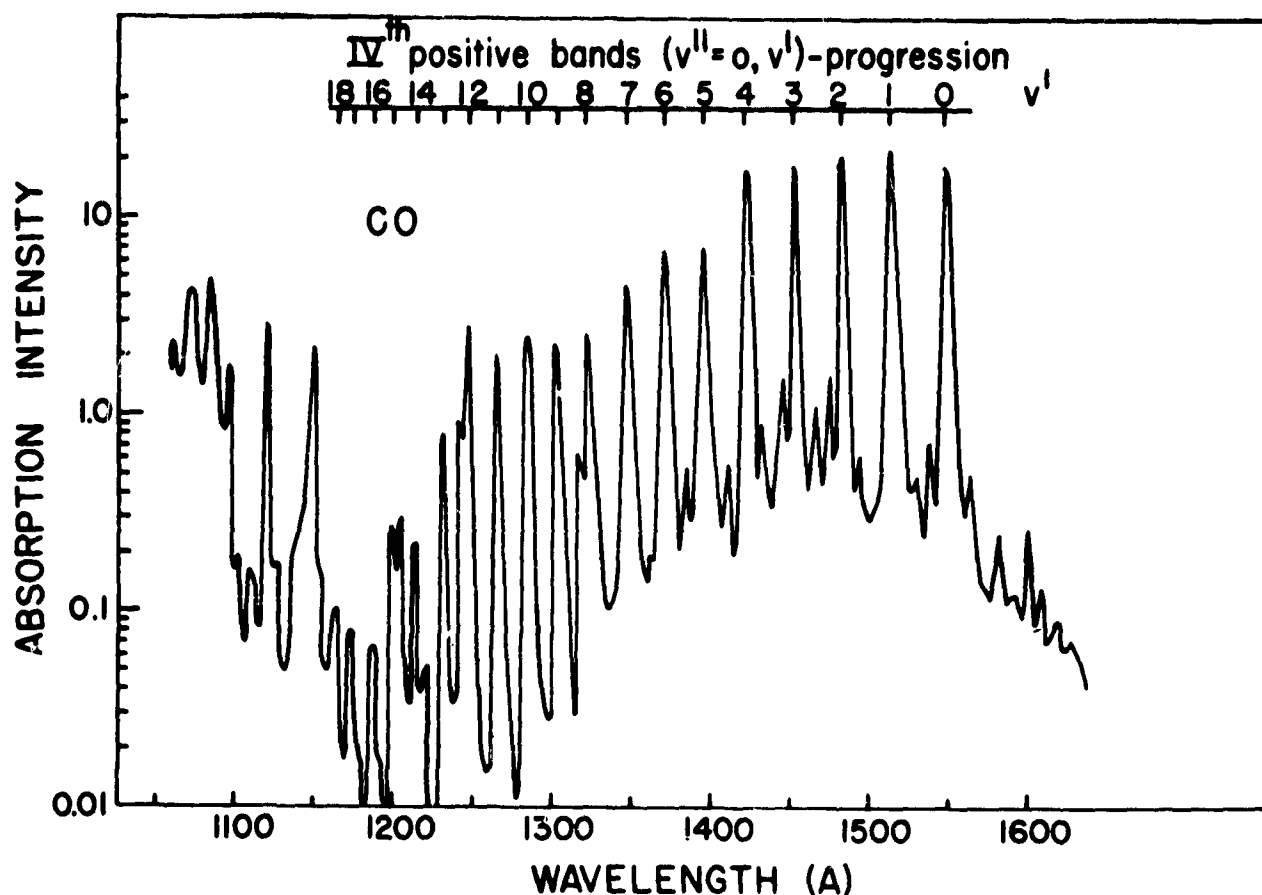
Fig. 25. Absorption curve of CO in the region from 1050 to 1650 Å.

apparent continuum in the region from 1300 to 1600 Å which appears high because of the contribution from the bands.

9.2. RESULTS FOR THE SPECTRAL REGION FROM 1060 TO 1170 Å

Several strong absorption bands were observed in this region. Most of them have rather symmetric intensity distribution, and their wavelengths agree well with those of the $X \rightarrow C$ and $X \rightarrow E$ transitions which were found by Hopfield and Birge (1927).

In this region, there appears to be a continuum beginning at about 1140 Å and its intensity is moderately strong at 1060 Å. It may be one of the dissociation continua of CO, and if so, the value 10.9 ev (or 1140 Å) would correspond to the upper limit of the dissociation energy of the ground state, $X\ ^1\Sigma^+$. This value is very close to the dissociation energy of the $X\ ^1\Sigma^+$ state (10.11 ev) proposed by Gaydon (1950), but the present data is not adequate to permit any conclusion.

In general, the data obtained for CO was unsatisfactory, and future measurements with higher resolution are considered.
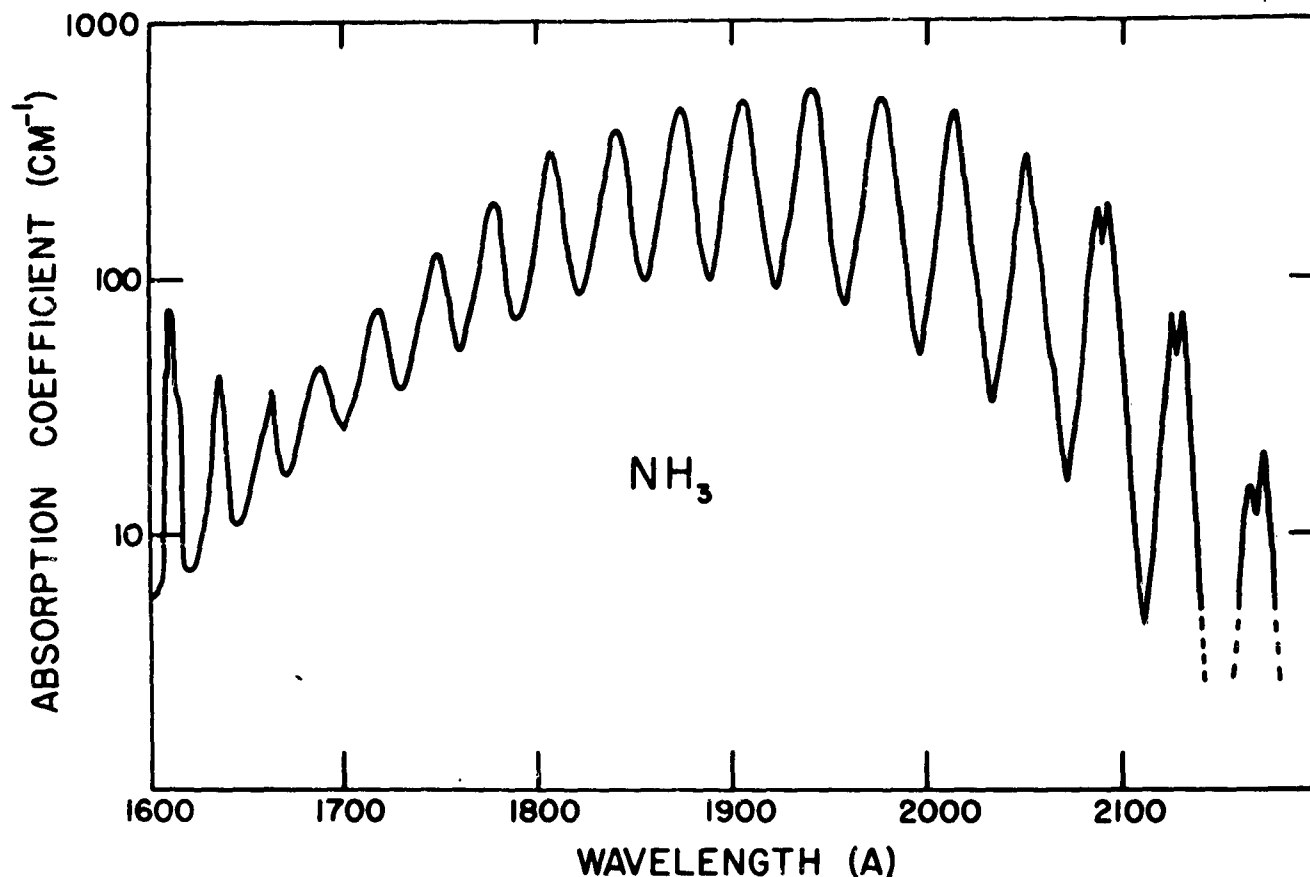
Fig. 26. The k-values of NH₃ in the region from 1600 to 2200 Å.

10. AMMONIA

The absorption spectrum of ammonia in the vacuum ultraviolet was most thoroughly studied by Duncan (1935, 1936 a). He confirmed the earlier observations of Leifson (1926) and Dixon (1933) in the longer wavelength region and extended their work down to 850 Å. The rotational structure of seven bands in the region from 1450 to 1620 Å belonging to the second excited state above normal was analyzed by Duncan and Harrison (1936) with a 21-ft focus vacuum spectrograph. There appear to be no k-values in the vacuum ultraviolet for NH₃ reported in the literature.

The ammonia gas was prepared from tank NH₃ by repeated fractional distillations, retaining only the middle fraction. Mass spectrometric analysis showed that the amount of impurities was less than the limit of detection (i.e., less than 0.05 percent).

Pressures of NH₃ used in the absorption cell were from about 0.02 mm to 15-mm Hg and were measured with two McLeod gauges. Although the compressibility of ammonia is comparatively high, the error from this cause was computed to be less than one percent. (See Farkas and Melville (1939).) The adsorption of NH₃ on the wall was more troublesome. There were some pressure variations during the absorption measurements, but, covering a limited range of spectrum at a time, the error from this source was kept below five percent. Adsorption of NH₃ on the LiF windows was detected by measuring the light intensity after the NH₃ was pumped out of the absorption cell, but the absorption due to the adsorbed NH₃ was very weak. As a rule, the k-values obtained for different pressures were consistent.
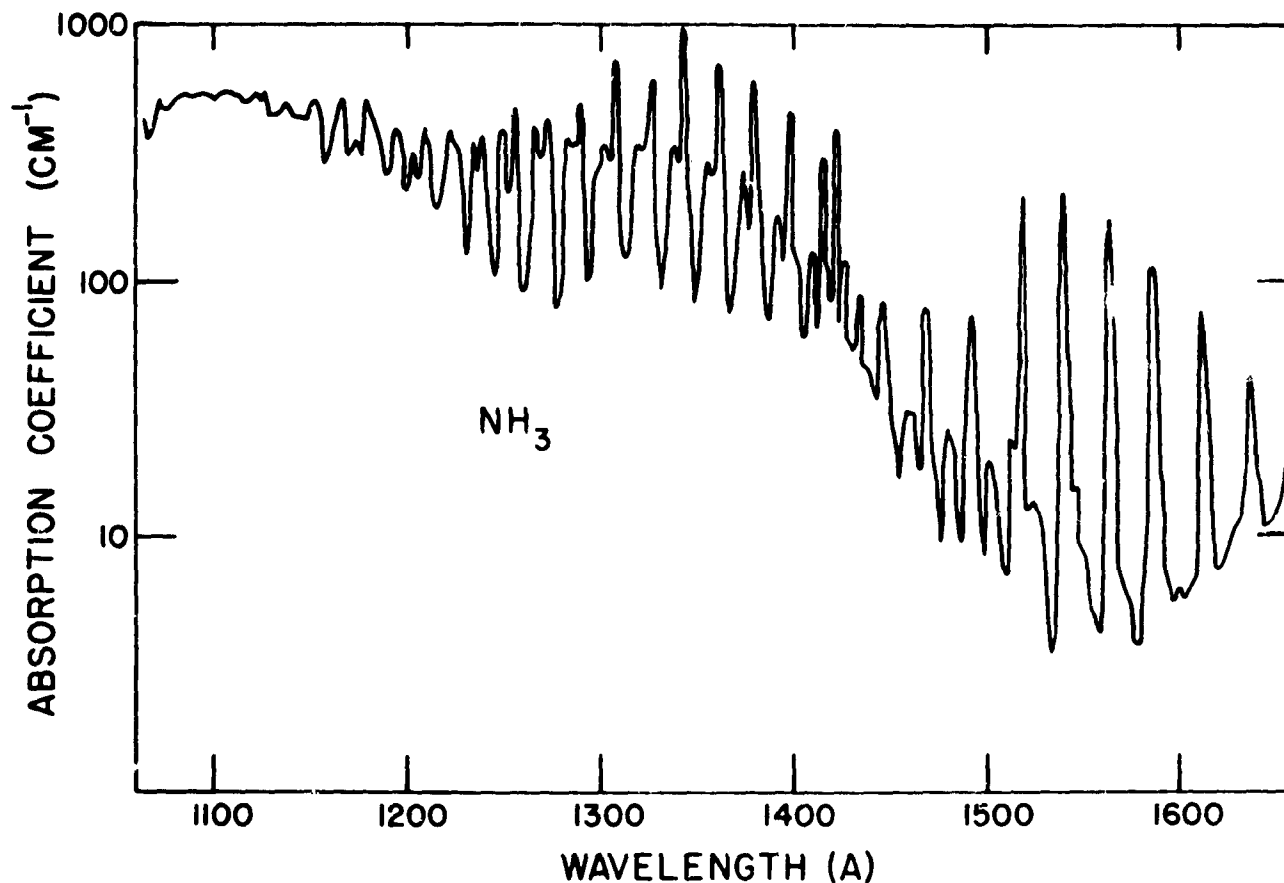
Fig. 27. The k-values of NH₃ in the region from 1050 to 1650 Å.

10.1. ABSORPTION COEFFICIENTS AND CONTINUA

Figures 26 and 27 show the k-values of NH₃ in the spectral region from 1050 to 2200 Å. The values are quite high throughout the spectral region, so that it was not necessary to use pressures of NH₃ higher than about 15 mm Hg. The highest k-value in this region was 980 cm⁻¹ at about 1342 Å. The k-value at Lyman alpha was 190 cm⁻¹. The bands in the region from 1300 to 1600 Å showed some apparent pressure effect.

There appear to be at least three continua underlying the numerous bands which extend over the entire spectral region. The first continuum is a rather broad and symmetric one which can be seen readily in Fig. 26 extending from about 1600 to 2200 Å. The f-value for this continuum with a maximum at about 1870 Å can be computed from the data by using Eq. (1), since the extrapolation of the wings of the continuum was comparatively simple. The f-value was found to be 0.030 (not including the bands).

The region below about 1550 Å (Fig. 27) is somewhat more complicated. A second continuum seems to cover the region from 1550 to 1200 Å with a maximum at about 1315 Å. The lower wavelength limit of this continuum is indefinite, since it overlaps the third continuum, and the f-value of the second continuum was estimated to be about 0.02.

The third continuum has a maximum at about 1100 Å. The present measurement did not reach far enough to the shorter wavelength end of this continuum, so the f-value cannot be determined accurately. A rough estimate would be about 0.1. The possibility that this continuum may be partly or largely due to photoionization will be discussed in Section 10.3.

10.2. BAND SYSTEMS

A comparison of the bands in Figs. 26 and 27 with those observed by Duncan (1935, 1936 a) shows good agreement with respect to the wavelengths and the relative sharpness or diffuseness of the bands. Duncan has already classified the bands into four different progressions, which he labeled Series I to IV, and has obtained series formulas for each progression. Duncan (1935) lists 15 bands in Series I (2170 to 1680 Å), 12 bands in Series II (1670 to 1390 Å), 13 bands in Series III (1440 to 1220 Å) and 4 bands in Series IV (1210 to 1160 Å). Nearly all of these bands were observed; however, the assignment of these bands to the four series, in a few instances, is not unambiguous in the present investigation.

According to Duncan, the frequency in all four v'-progressions involves only the ν_1 frequency and all four excited electronic states are of the same type as the ground state. The latter state has been designated by Mulliken (1935 a) as $^1A_1$. Duncan (1936 a) encountered a difficulty regarding the assignment of series II, and tentatively assigned it as a $^1A_1$ state and the three other electronic states as $^1A_1$ states.

Duncan (1935) observed that the maximum of intensity in all four series appeared at about $v' = 7$-9. This indicated that the "r_e" for the excited states are the same, although all are displaced from the "r_e" of the normal state by a considerable amount. From the data shown in Figs. 26 and 27, the maximum intensity seems to be at v' equal about 5 (using Duncan's assignment of v') for series I through III. In other words, the change in "r_e" for the excited states with respect to that of the ground state appears to be somewhat less than the result of Duncan. There appears to be an intensity anomaly between $v' = 6$ and $v' = 7$ in series II (see Fig. 27); however, this may be due to the separation of a secondary band head in $v' = 7$.

The bands in series I are quite broad and diffuse as compared with the bands in series II, III and IV. The diffuseness has been ascribed to predissociation by Bonhoeffer and Farkas (1927). The three bands (0,0, 1,0 and 2,0) at the long wavelength end of series I (see Fig. 27) are double-headed as found by Dixon (1933) and Duncan (1935), and the separation of the bandheads (~ 70 cm^{-1}) are also in agreement.

10.3. IONIZATION POTENTIAL OF NH₃

Using the four excited electronic states, Duncan (1936 a) attempted to obtain a Rydberg series converging to the first ionization potential of NH₃. He found, however, that the 0,0 bands of the four series did not fit a Rydberg series. By omitting series II and using the wave numbers of the most intense band of the remaining series, he obtained a formula converging to a limit at 11.5 ev. This value apparently agrees with the values obtained by the electron impact method; Mackay (1924), Waldie (1925) and Bartlett (1929) obtained 11.1, 11 and 11.2 ± 1.5 ev, respectively. Nevertheless, the formula obtained by Duncan appears to be unsatisfactory, since he omitted series II.

In order to determine the ionization potential, the method applied to NO (see Section 5.4) was used for NH₃. Using this method of measuring photoionization, the onset of ionization was found to be at 10.12 ±0.05 ev. This value agrees quite well with the most recent electron impact value obtained by Mann, Hustrulid and Tate (1940) of 10.5 ev ±0.1. Furthermore, the 0,0 member of series IV by Duncan lies at a wavelength (1207 Å) shorter than that for our value of the ionization potential (1225 Å). It is possible that series IV is part of series III and members beyond $v' = 12$ are preionized, thus appearing as a different series.

The continuum underlying the bands in the region below about 1225 Å must be due partly to photo-ionization. Since experiments on the ionization cross section have not been completed, the contribution of photoionization is not known.

A word may be added to the measurement of the ionization potential by the method used here. In the case of ethylene, the ionization potential by this method was found to be 10.46 ev. This is in agreement with the value of 10.45 ±0.03 from Rydberg series obtained by Price and Tutte (1940).

11. WATER VAPOR

At present, very little is known regarding the importance of water vapor in the region above the troposphere. The presence of this gas at high altitudes, up to at least 80 or 90 km, is known from observations of noctilucent clouds. The recent identification of the OH radical in the emission spectrum of the night sky by Meinel (1950) has aroused considerable interest in H_2O as a constituent in the high atmosphere. Bates and Nicolet (1950) made a theoretical study of the photochemistry of atmospheric water vapor for the altitude range from 60 to 100 km.

The absorption spectrum of H_2O vapor in the vacuum ultraviolet has been studied by several investigators. The early work of Leifson (1926) was extended by Rathenau (1933) and Henning (1932) down to shorter wavelengths. Later, Price (1936) observed two sets of Rydberg series in the region from 1000 to 1250 Å. One of these yielded an accurate value of the first ionization potential (12.56 ev) of water vapor.

Recently, Hopfield (1950) pointed out that water vapor may be important in the absorption of solar radiation, particularly in the region of Lyman alpha, and stressed the need for measurements of absorption coefficients. About the same time, Wilkinson and Johnston (1950) reported k-values of H_2O in the region from 1450 to 1850 Å. Below this region there appear to be no data except the measurement of Preston (1940) at 1215.6 Å.

The water vapor used in the present investigation was obtained from distilled water after repeated fractional distillation in a vacuum purification system at 0° C, retaining the middle fraction in each distillation. The fractional distillation was slow at this temperature but more effective in the removal of impurities than a similar process at a lower temperature. Mass spectrometric analysis of the water vapor showed no detectable amount of impurities.

Pressures of water vapor from 0.08 to 8 mm were used in the absorption cell. These pressures were measured with an alphatron gauge (National Research Corporation) which was calibrated against two McLeod gauges. Since the alphatron gauge reads the instantaneous pressure, it was particularly convenient for H_2O vapor which adsorbs strongly on the walls of the glass system. The water vapor was contained in a liter flask at a pressure somewhat below its vapor pressure at room temperature and released into the absorption cell whenever required. The adsorption of water vapor was so serious in some cases that it was necessary to allow the vapor to remain in the absorption cell for about an hour before absorption measurements were made. In spite of the precautions taken, the pressure during a run varied up to 10 percent and corrections were applied to the data.
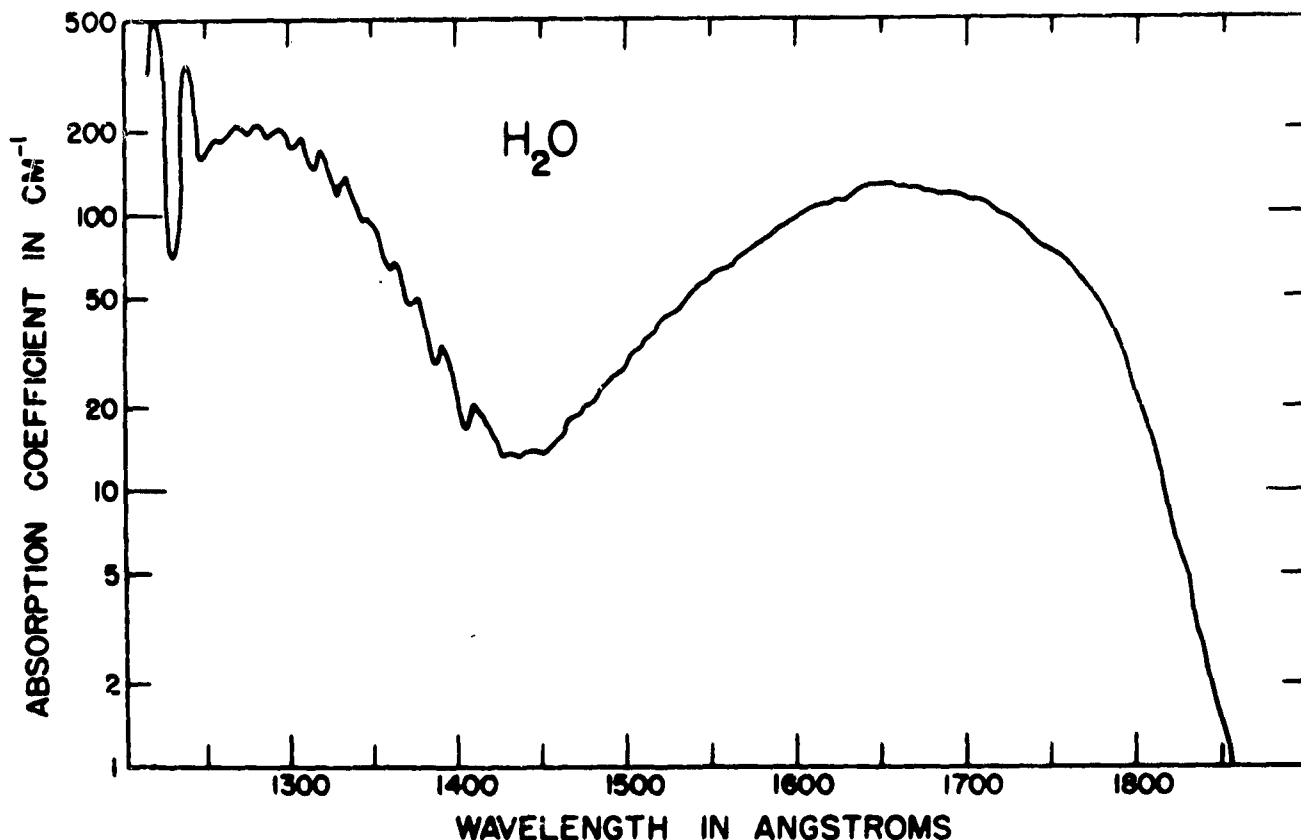
Fig. 28. The k-values of H₂O in the region from 1250 to 1850 Å.

11.1. RESULTS FOR THE SPECTRAL REGION FROM 1450 TO 1800 Å

The k-values of water vapor in this spectral region are shown in Fig. 28. The absorption here is almost entirely due to a continuum with a maximum at about 1655 Å. There are some indications of very weak bands in this region; however, the variations in the intensity are less than 5 percent, which is approximately the experimental error, so the presence of these bands is not certain. Rathenau (1933) reported seven weak bands in this region but the wavelength of most of these bands cannot be fitted with the "indications" mentioned above.

The k-value at the maximum of the continuum was 124 cm^{-1}. This value is about 10 percent higher than the value reported by Wilkinson and Johnston (1950). The k-values over the continuum are in fair agreement with their result; however, the three bands they reported were not found. Since the k-values of the minima between the peaks of the three bands are about 20 percent lower than the maximum k-value, these bands should be readily detected by the present method which appears to have better resolution and sensitivity to small variations in absorption intensity. The f-value for this continuum was found to be 0.041 as compared with 0.03 by Wilkinson and Johnston.

11.2. RESULTS FOR SPECTRAL REGION FROM 1250 TO 1450 Å

As shown in Fig. 28, a number of diffuse bands were found superimposed on a second continuum. The wavelengths of these bands are listed in Table 9, together with the bands observed by Rathenau (1933). The latter gave the wavelength range of the bands and not the wavelength of the maximum of each band. By using the wavelengths of the band centers, however, he obtained an interval of about 800 cm^{-1}. The results shown in Table 9 are in good agreement, considering the fact that these bands are diffuse and the heads of the bands cannot be measured accurately.

Table 9. Wavelengths (Å) of the diffuse bands of H$_2$O vapor in the region from 1250 to 1450 Å.

Rathenau	Present Observation
	1411
	1392
	1378
1361–1372	1364
1346–1357	1348
1332–1341	1335
1318–1324	1321
1306–1309	1308
1291–1297	1295
1279–1284	1281
1267–1271	1269
1253–1257	1257

The shorter wavelength limit of the continuum underlying the diffuse bands was estimated to be about 1150 Å. On this basis, the f-value of the continuum was found to be about 0.05.

11.3. RESULTS FOR THE SPECTRAL REGION FROM 1050 TO 1250 Å

The k-values of H$_2$O vapor in this spectral region are shown in Fig. 29. Here there are a number of strong bands, some of which are diffuse and others appear to have structure. Lyman alpha lies near the peak of one of the broad diffuse bands, and its k-value was found to be 387 cm^{-1}. This value is in excellent agreement with the value (390 cm^{-1}) obtained by Preston (1940).
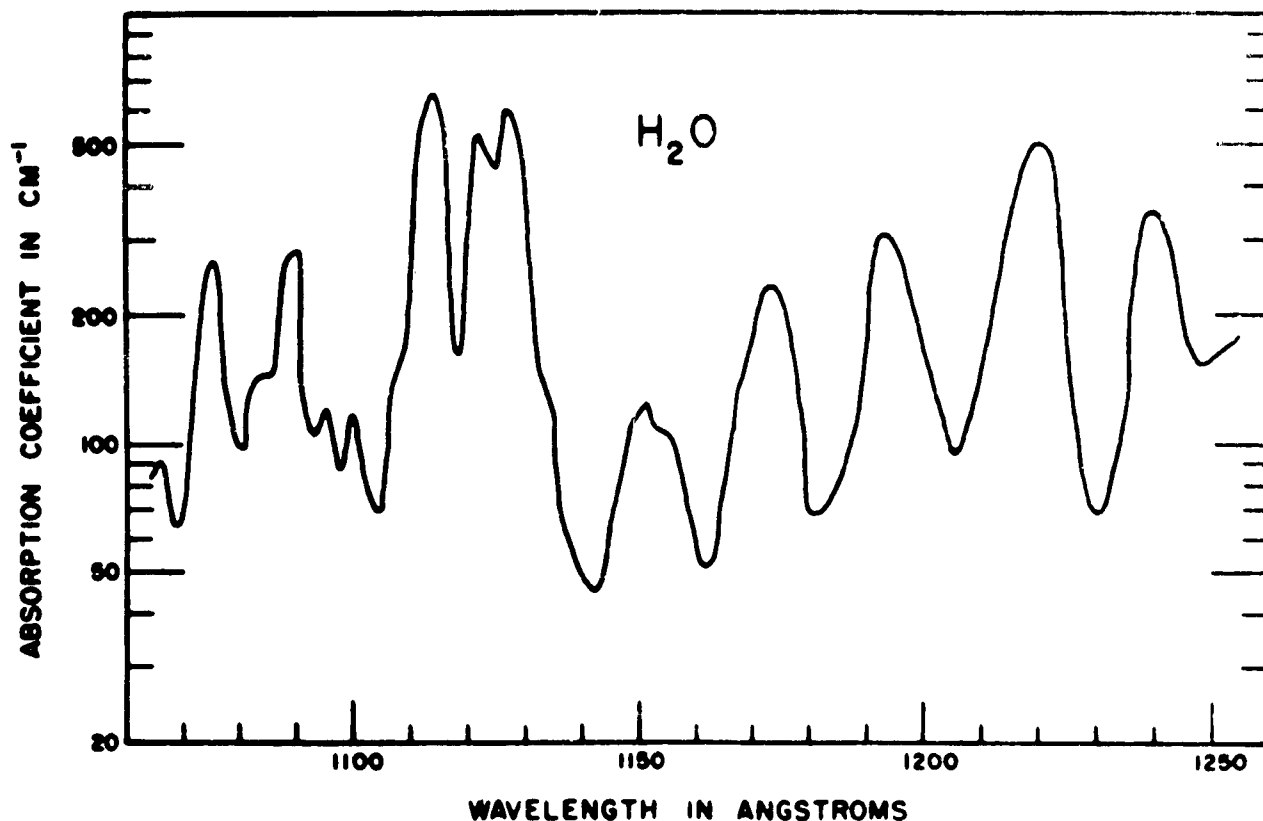
Fig. 29. The k-values of H₂O in the region from 1050 to 1250 Å.

Both Rathenau (1933) and Price (1936) studied this region. The latter, using higher dispersion, was able to resolve a great deal of the rotational structure but found it too complicated for complete analysis. In the present investigation, the k-values for the bands in the region below 1150 Å showed some "apparent pressure effect" which suggested that the bands were somewhat sharp and that the resolution used was not sufficient. However, the k-values of the bands in the region from 1150 to 1250 Å showed very little change with pressure and, hence, should be fairly reliable. A number of bands in this region were identified by Price (1936) as members of two Rydberg series. These bands appear in Fig. 29. The higher members of the series were not observed, since they lie beyond the transmission limit of LiF.

12. METHANE

The vacuum ultraviolet absorption spectrum of methane has been studied by several investigators. Leifson (1926) studied the region from 1215 to 1800 Å and found the absorption to be everywhere continuous, except for six bands between 1558 and 1420 Å. Rose (1933) was unable to find these bands and suggested that they appeared as a result of gaps in the band spectrum of hydrogen which Leifson used as background source. Duncan and Howe (1934), using as source a condensed discharge in hydrogen, which produces a true continuum, studied the methane spectrum down to 850 Å and concluded that the absorption
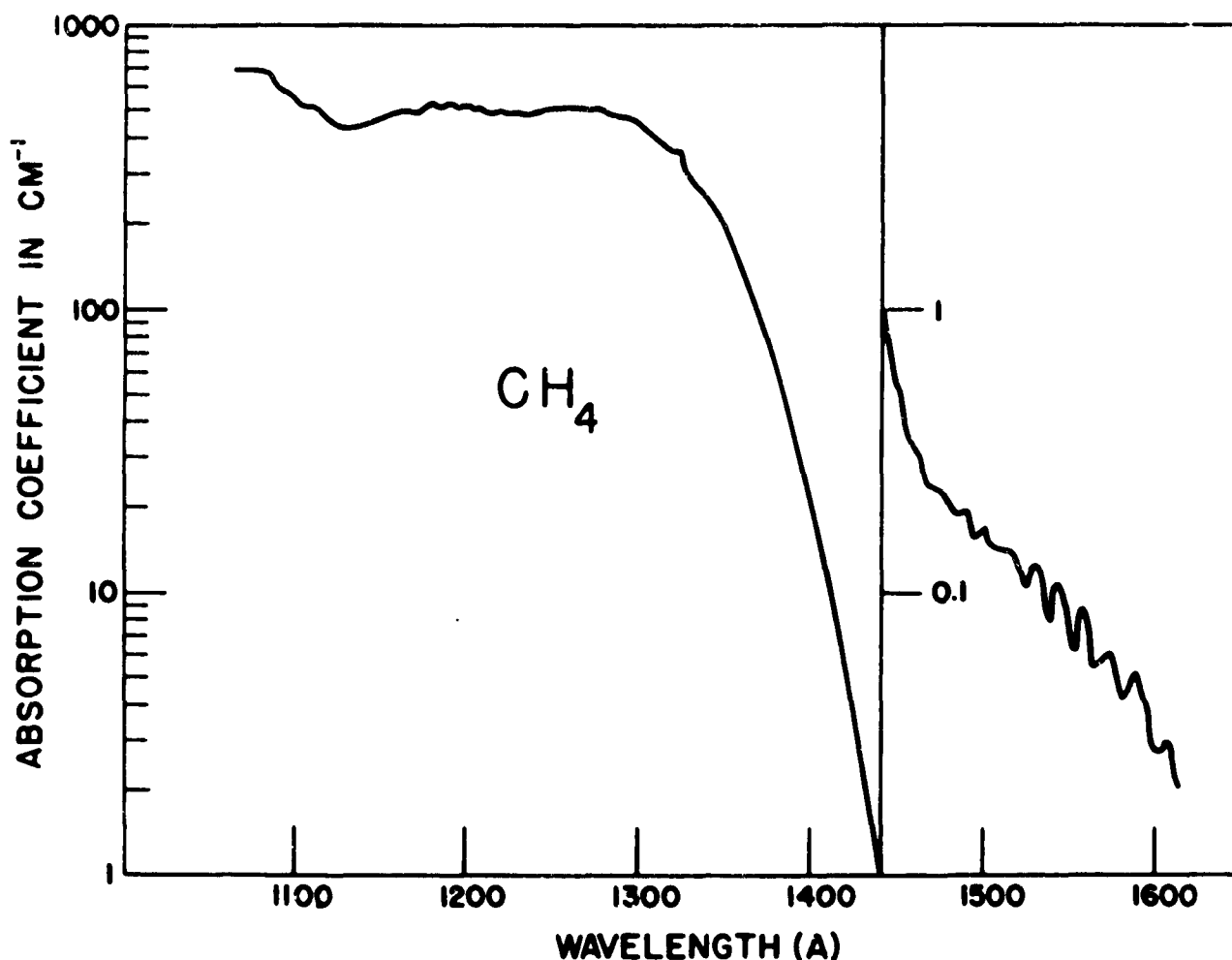
Fig. 30. The k-values of CH₄ in the region from 1050 to 1600 Å.

was continuous over the entire region. Absorption coefficients of methane in the region from 1370 to 1455 Å were measured by Wilkinson and Johnston (1950) who found a continuous rise of absorption intensity with decreasing wavelength. The present work deals with the absorption coefficients of methane between 1065 and 1610 Å.

The methane was purified from Matheson tank gas by repeated fractional distillation at liquid nitrogen temperatures, retaining only the middle portion of each distillate. Mass spectrometric analysis showed the purity to be greater than 99.5 percent with the impurity consisting almost entirely of ethane. No unsaturated hydrocarbons or higher paraffin hydrocarbons were detected, indicating that these substances could not comprise more than 0.05 percent of the total. The pressures of methane used in the absorption cell varied from 0.04 to 420 mm Hg.

12.1. ABSORPTION COEFFICIENTS

Figure 30 is a plot of k vs λ for methane between 1065 and 1610 Å. There appears to be continuous absorption over the entire range of observation, with some weak bands superimposed in some regions. Two

flat maxima and a possible third were observed. The first two lie at about 1260 Å and 1190 Å, both having k-values of about 500 cm^{-1}. The third at about 1075 Å, having a k-value of 700 cm^{-1}, is not certain, since this region is near the transmission limit of the LiF windows. The 1190 Å continuum seems to have super-imposed on it several relatively weak diffuse bands. Above 1450 Å there appear eleven bands that are also diffuse and weak.

Where comparisons can be made, the k-values agree with those of Wilkinson and Johnston (1950) only to a limited extent. At the lowest wavelength they measured (1370 Å), their value is about ten percent lower, but above 1400 Å the agreement grows steadily worse, their value being about an order of magnitude greater at 1440 Å. It is difficult to explain why they reported no k-values below about 1. With the cell length (38 cm) and pressure (40 cm) they used, $I_0/I = 2.7$ for a k-value of 0.05 cm^{-1}.

12.2. LONG WAVELENGTH LIMIT OF CH$_4$ ABSORPTION

The question of the long wavelength limit is not easy to answer. Wilkinson and Johnston (1950) give 1455 Å for this value. Since only one point is presented in evidence and no k-values below ~1 are given, one cannot help but feel that the result is open to question. The work of Duncan and Howe (1934) who found CH$_4$ absorption to 1450 Å is cited by Wilkinson and Johnston as evidence in support of the 1455 Å value. Duncan used a path length of 200 cm and a maximum CH$_4$ pressure of 1 mm Hg. With this layer thickness and an absorption coefficient of 0.1, $I_0/I = 1.01$; if $k = 0.5$, $I_0/I = 1.06$. Such small I_0/I ratios are very difficult to detect photographically and Duncan admits that his long wavelength limit might easily be in error, because of his low layer thickness, and that the value of 1850 Å found by Leifson (1926) and Rose (1933) independently, might be correct. Wilkinson and Johnston state that the oxygen impurity in CH$_4$ must be less than 0.00014 percent and that the continuous absorption up to about 1800 and 1869 Å observed by Leifson and Rose was presumed to be due to oxygen. The k-value of O$_2$ in this region has been measured in the present investigation and found to be of the order of 1 cm^{-1}. Therefore, using Leifson's layer thickness, attributing his absorption to oxygen would have required that his methane contain mostly oxygen rather than methane. This is deemed unlikely.

The long wavelength limit of absorption obtained in the present investigation is about 1650 Å. As compared to the photographic method, lower ratios of I_0/I can be measured by the photoelectric method since the photomultiplier current is linear with intensity. By careful measurements, k-values are fairly reliable even when I_0/I is as low as 1.05 and, therefore, in the case of methane, k-values as low as 0.02 cm^{-1} were measured with a cell length of 4.7 cm and CH$_4$ pressure of 420 mm Hg. The high value of the long wavelength limit obtained by Leifson may be attributed to photochemical decomposition of CH$_4$, since he placed the absorption cell near the light source. Photochemical products such as ethylene and acetylene absorb strongly at longer wavelengths. In this regard, the present work has shown that many gases have an absorption in the Schumann region which is comparable to that of O$_2$, and it is not safe to analyze only for O$_2$.

12.3. CONTINUA AND BANDS

As noted earlier, methane possesses two and possibly three regions of continuous absorption. One region has a maximum at about 1260 Å. This is in good agreement with the value of 1255.5 Å measured by

the dispersion techniques of Friberg (1927). Mulliken (1935 b) attributes this absorption to the transition $^1A_1 \rightarrow {}^1T_2((p) \rightarrow 3s)$. The second continuum having a maximum at 1190 Å has several comparatively weak bands superimposed on it. It is believed that these bands are real, since they contribute about 20 cm^{-1} to the k-value. This contribution is well outside the limit of error. No attempt has been made to classify these bands, since their diffuse character makes assignment of wavelength difficult. The approximate wavelengths are 1178, 1190, 1201, 1207, 1218 and 1230 Å. The question of these bands being due to impurities must be considered. The purity of the methane was carefully checked by mass spectrometric analysis and the only impurity found present in excess of 0.05 percent was ethane. Since these bands contribute about 20 cm^{-1} to a k-value of about 500 cm^{-1}, the impurity would have to comprise ～4 percent of the methane if its k-value were comparable at this wavelength. Alternatively, it would have to comprise 0.4 percent if its k-value were 5000 cm^{-1}. The most probable impurities remaining undetected are oxygen, water vapor and carbon dioxide, but since none of these fit the above requirements, their presence may be ruled out. That these bands may be due to ethane may be ruled out, since the strong absorption of ethane is primarily continuous and not banded as shown by Price (1935). In the region from 1462 to 1606 Å, eleven absorption bands were noted. Leifson has reported some of these, although Rose has pointed out that they might have been due to gaps in the hydrogen spectrum. Although this difficulty may arise photographically, it is unlikely that it will be encountered in photoelectric measurements, since light intensity is measured linearly. Similar considerations to those above may be used to eliminate impurities as the cause of these bands. The wave numbers are 62,260; 62,970; 63,530; 64,180; 64,810; 65,360; 66,010; 66,620; 67,200; 67,800 and 68,400 cm^{-1}. The frequency separation is about 600 cm^{-1} and the intensity seems to decrease as the region of continuous absorption is approached.

13. AN APPLICATION TO THE D LAYER

In this section an attempt is made to apply some of the absorption data to atmospheric physics. For this purpose, the D layer seems to be an appropriate subject, since the spectral range covered in the present investigation includes the atmospheric window in the region of Lyman alpha which has often been associated with the D layer.

Several processes have been suggested in the past for the formation of the D layer (see Introduction) and discussed by many investigators. For example, Bates and Seaton (1950) have evaluated the merits and defects of these theories on the basis of available data. Their paper provides the necessary background for the following discussion.

The photoionization of atomic sodium by solar ultraviolet in the region from 1800 to 2300 Å,

$$\text{Na} + h\nu \rightarrow \text{Na}^+ + e, \qquad (5)$$

has been proposed by Jouaust and Vassy (1941) and by Vassy and Vassy (1942). In this proposal, they rejected Prestor's (1940) k-value of O_2 at Lyman alpha and considered that solar radiation in the spectral region from 1100 to 1300 Å did not penetrate into the D layer. The data obtained in the present work agree completely with the k-values of all four gases at Lyman alpha obtained by Preston. Moreover, the k-values of the several windows of O_2 in the region from 1100 to 1200 Å have been found to be about the
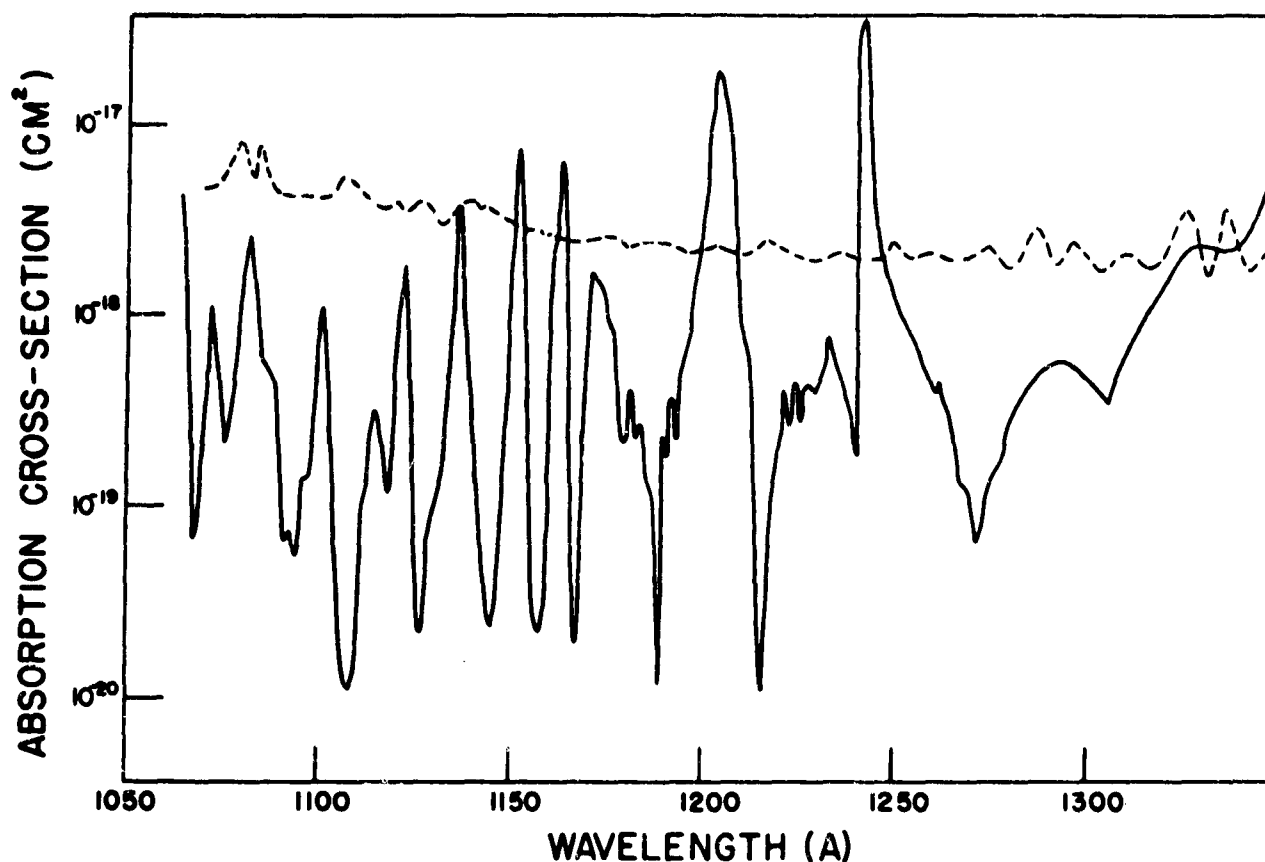
Fig. 31. Absorption cross sections of NO and O_2.

same as that of Lyman alpha. Regarding the photoionization rate of process (5), the estimates of Bates and Seaton were accepted in this discussion. Nicolet (1949), however, has considered that this process produces the normal D layer.

Of the several processes suggested for the formation of the D layer, the following appear to have the strongest support:

$$O_2 + h\nu \text{ (900 to 1000 Å, spectral region A)} \rightarrow O_2^+ + e \tag{6}$$

$$NO + h\nu \text{ (1100 to 1300 Å, spectral region B)} \rightarrow NO^+ + e. \tag{7}$$

Mitra (1951) has reported a detailed calculation to show that the D layer is produced by process (6), which was originally proposed by Mitra, Bhar, and Ghosh (1939). On the other hand, Bates and Seaton (1950) have shown that the D layer may very well be produced primarily by process (7) which was suggested earlier by Nicolet (1945). The latter, however, used process (7) to account for the increased ionization in the D layer during solar flares and not for the normal D layer.

Spectroscopic data seem to show that the D layer cannot be produced chiefly by process (6). As pointed out by Bates and Seaton, spectrograms by Hopfield (1946) show that a 4-mm layer of air completely absorbs radiation in spectral region A (see Eq. (6)). Tanaka (1953), who used a 3-m grazing incidence spectrograph and both the Lyman discharge and the helium continuum as source, confirms Hopfield's result, and estimates from pressures used that the windows in spectral region A are about two orders of magnitude

less transparent than those in region B. Price and Collins (1935) have observed an absorption continuum at 1100 Å which extends to shorter wavelengths with increasing intensity. Spectrograms by Hopfield and Tanaka also show this continuum.

The absorption intensity of O_2 down to 1060 Å is shown by the solid curve in Fig. 31 where the ordinate is expressed in cross section (cm^2). The continuum mentioned above appears at about 1100 Å and the cross section in the region from 1060 to 1100 Å is about $10^{-19}\,cm^2$. On the basis of the data obtained by Hopfield and Tanaka, the cross section should be still larger in region A which is utilized in process (6). A reasonable value for air in the spectral region A would be about $10^{-19}\,cm^2$ rather than $10^{-20} - 5 \times 10^{-22}$ which were used by Mitra (1951). If the higher value is accepted, process (6) would be placed in the lower E layer Thus, our data tend to confirm the conclusion of Bates and Seaton (1950).

In contrast, process (7) has the very attractive feature that NO can be ionized by Lyman alpha. This line has now been observed as a strong, solar emission line in a rocket spectrogram obtained by the University of Colorado (1953) at an altitude range within the D layer.

The concentration of atmospheric nitric oxide is not known. If the tentative estimate made by Bates and Seaton (1950) from a spectrogram obtained by Durand, Oberly and Tousey (1949) is the correct order of magnitude, our absorption data for NO seem to indicate that the major part of the production of the D layer can be attributed to process (7).

The absorption cross section of NO is also shown in Fig. 31 by the dashed curve. It represents a moderately strong absorption continuum with a number of weak diffuse bands. The experiment on photoionization described earlier showed that a major part of the NO absorption in this spectral region leads to photoionization. The data for the ionization cross section are not precise, but they do show that the cross section is much higher than was previously estimated. For example, the ionization cross section of NO in the appropriate region for process (7) is about 25 times larger than the estimate used by Bates and Seaton (1950).

The solar spectral intensity in the region from 1100 to 1300 Å is not known. However, Watanabe, Purcell and Tousey (1950) have estimated that the mean solar intensity in the spectral region from 1050 to 1240 Å corresponded to a black-body temperature of about 5200° K. This value is considerably lower than the 6000° K value assumed by Bates and Seaton. It is expected that rocket-flown experiments will soon provide reliable data on the solar spectrum and the distribution of atmospheric NO.

The data supporting the NO theory of the D layer are still insufficient. In spite of the considerable differences in the estimated and the experimental values of the parameters, the net result obtained by Bates and Seaton appears to be remarkably realistic.

14. ACKNOWLEDGMENTS

15. APPENDIX

TABLES OF ABSORPTION COEFFICIENTS

Tables (10 through 14) of k-values of O_2, NO, CO_2, N_2O and H_2O have been included in the Appendix, since in some cases they may be more convenient than the corresponding intensity curves. The data cover only those spectral regions in which the k-values are independent of pressure, or nearly so (i.e., the region of continuous absorption and very diffuse bands). The k-values are averages of several values (different pressures). Although the wavelengths are read to the nearest 0.5 or 1 Å, they may be in error by 1 or 2 Å.

Table 10. The k-values for O₂ in the region from 1160 to 1750 Å.

λ	k	λ	k	λ	k	λ	k
1166	0.5	1230	10	1336.5	59.1	1547	217
68	1.0	31.5	13	39.5	60 3	51	209
69	2.1	32.5	14	43	75	55.5	204
72	44	33.5	20	45	93	62.5	194
74.5	38	34.5	20	49	155	69.5	175
75	36	35	12.3	51	191	72	171
76	24	36	14	55	191	77.5	165
77	23	37.5	13	61	220	81	158
78	11	38.5	9.3	66	259	85.5	155
80.5	5.6	39.5	8.1	69	303	89	144
81.5	11	40	6.3	75	332	91	137
82.5	6.1	40.5	4.9	78	342	96	133
84	7.1	41.5	870	84	354	160?	125
86	3.9	43.5	940	91.5	359	08	112
88	2.8	45	95	94	366	13	104
88.5	2.9	47	56	1400.5	370	20.5	92
89.5	0.4	49.5	39	05	375	23.5	89
90	6.2	52	28	08	376	28.5	80
91.5	5.0	54.5	23	10.5	380	33.5	75
92.5	10.1	56	19	18	380	36.5	72
93	6.7	57	16	27	376	38.5	69
94.5	12.7	59.5	12.5	30	375	44	63
95.5	16.5	60.5	10.8	33	377	48	60
98	32	62	11.9	36	375	54	54
1200	51	63.5	9.2	40.5	371	58.5	49
01.5	90	64.5	6.5	43.5	372	63	46
02	104	66	4.9	50	370	67	42
03.5	230	69	3.2	55	368	71	39
05	500	71	1.8	57.5	365	77.5	35
06	480	74	2.5	60	361	82	32
06.5	460	77	4.1	63	355	87	30
08.5	330	79.5	6.7	67.5	355	89	26.5
09	130	83.5	9.8	73.5	350	97	24.0
10	87	87	12.7	79	338	1702	21.8
11	24	90.5	14.6	86	324	05	20.3
13	17	93	15.7	89	318	12	18.2
13.5	11	96.5	14.8	91.5	319	17	16.4
15.6	0.3	99	14.0	95	307	22	15.0
17.5	0.8	1302	11.9	99	304	27	13.6
18.5	2.5	06	9.6	1504	294	32	11.9
20	5.2	09	13.9	10.5	285	37	10.6
21	5.9	12.5	19.4	17	274	42	9.5
22	11	17	29.6	22.5	266	47	8.3
23.5	7.0	21.5	42.9	32	249	49	7.2
25	13	25	55.0	37.5	233	51	6.5
28.5	11	29	62.1	41.5	227		
29	12	33.5	61.6	44.5	219		

Table 11. The k-values for NO in the region from 1060 to 1360 Å.

λ	k	λ	k	λ	k	λ	k
1069	134	1140	113	1222	60	1300	58
71	156	41	95	24	57	02	53
75	176	42	98	26	55	03	48
78	214	43	101	31	52	04	45
80	233	46	91	35	58	05	51
83	176	50	84	37	56	08	53
85	215	52	80	40	54	10	57
88	146	55	75	43	53	12	58
91	129	57	79	45	53	14	54
93	126	58	71	48	55	16	48
95	129	62	70	50	67	18	47
99	114	66	69	55	52	20	52
1101	120	67	68	57	54	22	77
05	129	70	67	58	57	25	87
07	173	72	71	61	59	27	94
08	170	73	72	63	54	29	80
10	151	77	68	65	51	31	56
13	116	80	65	67	53	32	45
15	105	82	63	70	58	34	53
16	105	84	59	72	58	35	83
19	98	86	66	75	63	37	90
21	108	90	64	78	51	38	82
23	93	92	66	79	48	39	65
25	98	93	60	81	47	41	56
26	110	97	58	83	58	43	42
29	101	99	59	84	62	45	46
32	79	1202	62	87	77	46	53
33	82	04	62	88	76	48	59
34	82	07	57	91	67	50	56
35	92	10	57	92	49	52	57
36	90	12	59	93	50	54	42
37	103	14	58	94	55	56	40
38	106	15.6	68	96	65	58	32
39	108	19	61	98	63	61	85

Table 12. The k-values for CO₂ in the region from 1060 to 1750 Å.

λ	k	λ	k	λ	k	λ	k	λ	k	λ	k	λ	k	λ	k
1064	250	1159	13.5	1251.5	7.1	1344.5	23	1423.5	18.2	1512	12.6	1591	4.8	1673.5	1.45
68	430	61.5	9.1	53.5	7.5	46	19.2	25.5	18.3	14.5	13.0	93.5	4.6	74.5	1.51
71	480	63.5	6.8	55.5	5.7	48	29	28	14.5	16	13.9	96	6.0	77.5	1.43
74.5	450	65.5	17.0	57	5.8	51.5	22	30.5	14.3	17	14.6	99	5.0	79.5	1.25
76.5	220	67.5	16.6	60	10.8	53.5	17.1	33.5	16.0	18.5	13.6	1602.5	4.4	81.5	1.15
79.5	350	68.5	6.8	61.5	10.1	54.5	17.4	35.5	16.8	19.5	13.9	04.5	4.5	83.5	0.97
82.5	330	69.5	5.1	64	9.2	56.5	16.7	37	17.3	21	12.5	06.5	3.9	84	0.78
84	200	71	3.2	67	7.7	57.5	18.1	38.5	15.0	23	11.7	08	3.7	85.5	0.97
87.5	3620	72.5	3.6	68.5	12.4	60	27	41.5	14.9	24.5	11.8	10.5	4.4	86.5	0.90
89.5	470	73.5	6.8	71	14.3	62.5	21	44	16.0	26.5	12.0	12	4.2	88.5	0.72
92	200	76	6.7	73.5	12.3	64	17.0	46.5	17.4	28.5	11.9	13.5	4.1	90	0.89
92.5	240	78	1.37	76.5	8.9	66.5	17.4	48	16.9	30.5	12.8	16	4.1	91	0.93
94	156	79.5	1.33	78	11.2	68	17.4	51	15.7	32	12.5	16.5	3.7	93.5	0.73
96	154	81	1.22	79	14.4	70	21	53	14.7	33.5	11.5	18	3.5	95.5	0.75
99	230	83	2.6	81	17.2	72	17.8	55.5	15.0	36	10.5	21	3.3	97	0.66
1101	320	85.5	1.89	83	18.1	73	18.3	57	16.5	38.5	9.8	23.5	2.7	99	0.63
02.5	310	89.5	0.75	84.5	15.1	75	16.1	58.5	18.5	40.5	10.7	25.5	3.3	1702	0.57
04.5	330	91	0.99	86.5	11.4	77	15.0	61	15.9	43	11.6	28.5	3.2	05.5	0.51
06.5	410	92.5	1.15	87.5	11.2	78	15.6	63.5	13.5	46	9.7	30.5	3.2	08	0.52
08	600	97	0.94	88.5	12.9	81	20.4	65	13.7	47	10.0	31.5	2.69	10	0.51
10	1020	98.5	0.99	89.5	14.6	83	18.1	66	15.0	48.5	10.2	34	2.35	12.5	0.39
11	900	1201.5	1.22	90.5	22	84.5	17.2	68	17.8	50	8.5	34.5	2.35	15	0.47
14.5	1220	03	1.34	91.5	25	86.5	16.7	69.5	18.0	51.5	8.6	36.5	2.23	17	0.33
16	1630	06	1.24	93.5	23	88	15.4	71.5	16.2	53.5	8.4	38.5	2.27	19.5	0.43
18	3660	08.5	1.46	95.5	17.3	91.5	15.3	73.5	14.1	54.5	10.0	40.5	2.17	21.5	0.34
19	4350	09.5	1.69	97	13.7	94.5	15.7	75	14	56	9.9	41.5	2.18	24	0.39
20	3780	10.5	1.54	1300	15.9	97	13.5	77.5	15.8	58.5	9.2	43	2.39	27	0.30
21.5	1900	11.5	1.64	02.5	34	98	14.6	79	14.9	60	9.3	44.5	2.25	29.5	0.28
24	1630	13	1.83	05.5	22	99.5	16.2	80.5	15.6	62	8.1	45.5	2.33	32	0.25
26	2470	15.6	1.97	07.5	16.2	1401	17.0	82.5	17.1	63	7.8	47.5	2.15	34.5	0.26
28.5	2520	18.5	1.99	11.5	17.5	03	17.4	84.5	15.3	66.5	7.7	49.5	1.76	37	0.21
32	640	21	2.10	13	31	05	15.5	88	14.5	68.5	7.9	50.5	1.77	40	0.22
36.5	340	23	2.15	15.5	25.8	06.5	14.3	90.5	14.0	71.5	7.9	54	1.47	42.5	0.22
38	182	24	2.44	19.5	19.5	08	15.4	93	16.3	74	6.4	56.5	1.63	47	0.17
42	510	26.5	2.78	23.5	25	09	15.5	95.5	16.1	77	5.8	57.5	1.60	52	0.15
46	74	30	2.83	25.5	31	11	16.8	96.5	15.9	78.5	6.1	60	1.74		
49	104	35.5	3.4	27.5	27	13.5	16.1	98.5	15.0	80.5	6.6	63	1.66		
51.5	56	39.5	4.2	31.5	20	15.5	16.0	1501	12.5	83.5	7.1	65	1.42		
52	102	43.5	5.3	34.5	25	16.5	16.1	03	14.9	85.5	6.0	67.5	1.41		
55	17	46	4.3	36.5	32	18.0	17.3	06	15.9	87.5	5.9	69	1.55		
56	73	47.5	5.5	39.5	24	20.5	15.6	07.5	14.9	88.5	5.7	70.5	1.25		
58	108	50	7.2	43	19.1	21.5	18.1	09	14.7	90	5.0	72	1.27		

Table 13. The k values for N₂O in the region from 1080 to 2160 Å.

λ	k	λ	k	λ	k	λ	k	λ	k	λ	k	λ	k	λ	k
1082	880	1182	400	1283	2470	1385.5	19	1481	87	1553.5	2.6	1626	1.29	1827	3.80
87	1150	85	280	85.5	2430	87	19.5	84	72	57	2.2	28.5	1.19	37	3.83
89.5	1370	89	126	87	2370	90.5	20.5	86.5	81	59	2.1	30.5	1.27	47	3.70
91.5	1200	90	112	88	2330	94	21.3	88	99	63	3.4	34	1.30	57	3.59
93.5	850	92	104	90	2390	96	24.5	89	101	64	2.9	35.5	1.41	67	3.56
95.5	690	96	84	92	2590	98.5	28	91	84	67.5	1.60	36	1.28	77	3.43
97	920	98	83	93	2260	1402	30	92	72	68.5	1.38	37	1.41	87	3.27
98	1350	1201	72	97	2190	05	39	93	62	70	1.32	39	1.26	97	3.15
1100.5	1450	02.5	67	99.5	2060	07	44	95	47	72	1.27	40	1.35	1907	2.89
04.5	1270	05	65	1302	1920	10	47	99.5	42	74	1.11	44	1.42	17	2.75
07	1270	09	74	07	1670	13	56	1501	58	74.5	1.14	47	1.51	27	2.59
09	1020	11	70	11	1490	16	76	02	60	75.5	1.07	49.5	1.51	37	2.33
12	750	15.6	66	12	1340	18	72	04.5	39	77.5	1.09	51.5	1.60	40	2.21
15.5	680	18	68	15	1160	20	75	08.5	25	79.5	1.48	52.5	1.66	47	2.16
18	900	22	84	17	108ᵉ	22	85	11	23	81	1.64	54	1.59	50	2.00
20	790	23	87	19	920	23	98	12	26	83	1.37	56.5	1.66	57	1.89
22	560	25.5	112	23	850	24.5	108	15	25	84	1.26	57.5	1.59	60	1.79
24	490	29.5	133	27	630	28	114	16	27	85.5	1.08	60	1.63	67	1.84
26.5	590	34.5	188	31	560	30	107	18	25	87	0.95	62.5	1.75	70	1.61
33	930	39	272	32	520	31.5	124	21	15.7	89	0.88	64.5	1.84	77	1.61
32	740	42.5	390	35.5	410	33	152	23	11.8	90	0.88	67	1.87	80	1.42
35.5	490	46.5	520	37	350	34	162	25	10.3	91.5	0.88	69	1.81	90	1.27
41	620	49	610	38	330	36	156	26	11.1	93	0.90	71	1.89	2000	1.10
45	600	51.5	730	40	300	39.5	145	28.5	13.4	93.5	0.96	73.5	1.84	10	0.96
48	520	53	810	42	260	41	141	32	10.6	94.5	0.82	74.5	1.86	20	0.84
51	610	55	930	43.5	220	43.5	209	34	9.7	96	0.89	77	1.98	30	0.70
52.5	730	56.5	1000	45	198	46	205	35	8.5	98	1.03	87	2.15	40	0.59
53.5	810	61	1330	47	175	48	152	36	7.6	99	1.11	97	2.31	50	0.50
55.5	930	63	1450	50	130	50.5	147	37.5	5.9	1600	1.11	1707	2.46	60	0.42
57	1000	64	1470	53	103	52	177	39	5.3	02	1.10	17	2.65	70	0.35
61	1330	65	1610	54.5	88	55	242	39.5	4.8	04.5	0.99	27	2.91	80	0.29
62	1450	69	1810	57	74	58	169	40	4.6	08	1.01	37	3.00	90	0.24
63	1470	71	1950	61	53	60.5	137	41.5	4.6	12	1.06	47	3.08	2100	0.19
66	1610	73	2050	63	47	63.5	153	43	5.6	13	1.66	57	3.34	10	0.15
68.5	1810	74	2160	67	32	66	224	45	7	15.5	1.03	67	3.46	20	0.12
72	1950	75	2100	70.5	27.1	68	148	46	6.2	16.5	1.05	77	3.52	30	0.11
75	2050	76.5	2320	74	22.3	70	115	47	5.1	18	1.05	87	3.75	40	0.09
77.5	2490	78	2280	76	21.2	74	124	49	4.2	21	1.03	97	3.72	50	0.07
79	2320	79.5	2330	80	19.5	76.5	164	50.5	3.4	23.5	1.25	1807	3.77	60	0.05
80	770	82	2430	82.5	18.7	80	102	52	3.3	25	1.25	17	3.83		

Table 14. The k-values for H_2O in the region from 1065 to 1850 Å.

λ	k	λ	k	λ	k	λ	k	λ	k	λ	k	λ	k	λ	k
1065	88	1149	114	1230	69	1308	187	1379.5	45	1470	18.1	1572.5	73	1672	122
66	91	50	115	34	108	09.5	180	81	42	71.5	18.5	75	75	75	119
68.5	65	51	123	36	260	11.5	161	83.5	35	74	19.1	78	78	80	119
70.5	78	52.5	111	39	350	13	150	86	30	76.5	20.1	80	78	85	114
71.5	115	53.5	107	43	260	14.5	144	88	28	78	20.3	81.5	79	90	114
73.5	188	55	105	44	205	15.5	143	89.5	30	80	20.4	84.5	82	95	114
75.5	260	57.5	84	47.5	153	18	157	91	31	82	21.1	86	84	1700	111
77	188	61	56	49.5	158	19.5	169	92	33	84	22.4	87	84	06.5	110
80.5	96	63.5	66	52.5	168	21.5	165	94	32	87	23.4	89.5	88	10	107
81.5	130	65	78	54	175	23.5	149	95	30	89.5	23.9	91.5	89	15	106
83	141	66	98	56	183	25	137	96.5	29	92	25.2	93.5	90	20	99
86.5	147	68	146	57.5	185	27	125	99.5	24	95.5	26.4	96.5	92	25	95
88.5	270	69	153	60	183	28.5	114	1400.5	21	98	27.9	99.5	95	30	91
90.5	280	70.5	198	62	183	29.5	116	03	17.8	1500	28.9	1602.5	98	35	85
91	134	72	230	64	194	31.5	128	06	16.5	02.5	30.4	05	99	40	78
93	103	73	230	66	198	32.5	128	07.5	17.4	05	32	08	103	45	74
95.5	120	75.5	200	70	209	34.5	134	09.5	19.4	09	34	12	103	50	70
98	86	78	138	72	201	36	128	11	20.2	11.5	35	13	104	55	68
1100	115	79	104	73.5	197	37	121	13.5	19	12.5	36	16.5	107	60	64
02.5	83	80.5	68	74.5	193	38.5	114	16	17.9	15.5	36	18.5	108	65	58
04	70	82.5	70	75.5	195	40.5	106	18.5	16.6	18	38	21	109	70	54
06	91	85.5	89	77.5	201	42.5	99	20.5	15.4	21.5	40	23.5	111	75	49
08	132	89.5	132	78.5	203	44	93	23.5	14.4	23.5	42	26	111	80	43
09.5	180	90.5	240	80	210	46	95	25	13.3	2?	44	28.5	111	85	39
11.5	490	92.5	310	81.5	209	47.5	96	28	13	29	45	30.5	113	90	33
14.5	650	95.5	270	83	209	49	93	30.5	13.2	32.5	47	32	115	95	26
16.5	400	96.5	240	84	208	51	90	33.5	13.2	35	48	34	117	1800	21
18.5	161	98.5	193	86	199	52	87	37	13	38	50	36.5	120	05	17
20.5	440	1202	135	87.5	189	54	85	40	13.2	40	52	39	122	10	13
22	520	03	115	89	189	55.5	78	41.5	13.5	42	53	40	120	15	10
23.5	470	05	95	91	192	58	67	44	13.5	45	55	43	121	20	7.7
25.5	440	08	123	92.5	196	59	64	46.5	13.7	48	57	44.5	123	25	5.9
27	590	10	166	94	202	61.5	61	49	13.6	51	59	47.5	125	30	4.6
28.5	530	11	182	96	198	63.5	66	50.5	13.6	54	61	50	124	35	3.4
32.5	157	13	270	98	192	65.5	64	52.5	13.4	57	63	52	123	40	2.6
35	114	15.6	387	99	185	67	61	55.5	14.3	59.5	63	54.5	127	45	1.8
37	64	18.5	490	1300	178	68	56	58	14.9	63	64	58	122	50	1.5
40	49	21	490	01.5	173	69.5	52	61	15.5	64.5	64	60	122	55	1.0
42	45	22.5	410	03	171	71.5	46	64	17	66.5	70	63	123		
46	75	23.5	320	05	173	74.5	47	66	17.7	68	69	65	122		
48	99	26	123	06	181	77.5	49	68	18.1	70	71	68	121		

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